

PCT COOPERATION TREATY

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Assistant Commissioner for Patents
United States Patent and Trademark
Office
Box PCT
Washington, D.C. 20231
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 03 August 2000 (03.08.00)	
International application No. PCT/IL99/00681	Applicant's or agent's file reference 121822.1 MM
International filing date (day/month/year) 15 December 1999 (15.12.99)	Priority date (day/month/year) 15 December 1998 (15.12.98)
Applicant EIN-ELI, Yair et al	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:
03 July 2000 (03.07.00)

☐ in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was
☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

<p>The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland</p> <p>Facsimile No.: (41-22) 740.14.35</p>	<p>Authorized officer Claudio Borton</p> <p>Telephone No.: (41-22) 338.83.38</p>
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PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference 121822.1 MM	FOR FURTHER ACTION see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. PCT/IL 99/ 00681	International filing date (day/month/year) 15/12/1999	(Earliest) Priority Date (day/month/year) 15/12/1998
Applicant ELECTRIC FUEL LIMITED et al.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

☐ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☒ because this figure better characterizes the invention.

7

☐ None of the figures.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/IL 99/00681

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 H01M12/06 H01M4/62 H01M8/22 H01M4/90

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	DE 30 25 476 A (GOULD INC., ROLLING MEADOWS, US) 12 February 1981 (1981-02-12)	1, 2, 7, 9, 10, 16, 18, 19
A	page 12, line 17 -page 17, line 3 figure 1	24
Y	--- PATENT ABSTRACTS OF JAPAN vol. 010, no. 087 (E-393), 5 April 1986 (1986-04-05) & JP 60 230359 A (PENTEL KK), 15 November 1985 (1985-11-15) abstract	1, 2, 7, 9, 10, 16, 18, 19
A	--- -/-	11-14, 20-24, 30-37, 39, 40



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

2 March 2000

Date of mailing of the international search report

13/03/2000

Name and mailing address of the ISA

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/IL 99/00681

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	DE 36 13 237 A (DURACELL INT., TARRYTOWN, US) 4 December 1986 (1986-12-04) page 3, line 1 - line 4 page 4, line 21 - page 6, line 10 page 10, line 12 - line 27	1-3, 7, 9, 10, 16, 18, 19
A	---	24
Y	DATABASE WPI Section Ch, Week 198152 Derwent Publications Ltd., London, GB; Class L03, AN 1981-95576D XP002131855 & JP 56 145669 A (MATSUSHITA ELEC IND CO LTD), 12 November 1981 (1981-11-12) abstract	1-3, 7, 9, 10, 16, 18, 19
A	---	11-14, 20-24, 30-37, 39, 40
A	DATABASE WPI Section Ch, Week 198540 Derwent Publications Ltd., London, GB; Class L03, AN 1985-246787 XP002131856 & JP 60 163367 A (MATSUSHITA ELEC IND CO LTD), 26 August 1985 (1985-08-26) abstract	1, 2, 4, 9, 10, 16, 18, 19, 21, 23, 27
A	---	1, 16, 30
A	PATENT ABSTRACTS OF JAPAN vol. 008, no. 272 (E-284), 13 December 1984 (1984-12-13) & JP 59 143282 A (MATSUSHITA DENKI SANGYO KK), 16 August 1984 (1984-08-16) abstract	
A	---	15, 25, 41
A	US 5 232 798 A (GOLDSTEIN JONATHAN ET AL, JERUSALEM, IL) 3 August 1993 (1993-08-03) claim 1	
A	---	8, 17
	EP 0 551 204 A (ELECTRIC FUEL LTD, JERUSALEM, IL) 14 July 1993 (1993-07-14) column 8, line 49 - column 9, line 9	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/IL 99/00681

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 3025476 - A	12-02-1981	FR 2462784 A GB 2059141 A JP 56022055 A	13-02-1981 15-04-1981 02-03-1981
JP 60230359 - A	15-11-1985	NONE	
DE 3613237 - A	04-12-1986	US 4585710 A AU 574315 B AU 5550186 A BE 904576 A BR 8601709 A CA 1271216 A CH 671484 A DK 182686 A ES 554197 A FR 2580867 A GB 2174534 A,B IE 57298 B IT 1190322 B JP 2065787 C JP 7032030 B JP 61248371 A MX 164749 B NL 8600928 A NO 861567 A,B, SE 464998 B SE 8601823 A ZA 8602426 A	29-04-1986 30-06-1988 30-10-1986 10-10-1986 16-12-1986 03-07-1990 31-08-1989 23-10-1986 16-07-1987 24-10-1986 05-11-1986 15-07-1992 16-02-1988 24-06-1996 10-04-1995 05-11-1986 22-09-1992 17-11-1986 23-10-1986 08-07-1991 23-10-1986 25-11-1987
JP 56145669 A	12-11-1981	NONE	
JP 60163367 A	26-08-1985	NONE	
JP 59143282 A	16-08-1984	NONE	
US 5232798 A	03-08-1993	NONE	
EP 0551204 - A	14-07-1993	IL 100625 A AT 146625 T DE 69306598 D DE 69306598 T ES 2097975 T US 5318861 A	30-03-1995 15-01-1997 30-01-1997 12-06-1997 16-04-1997 07-06-1994

PATENT COOPERATION TREATY

From the:
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:
REINHOLD COHN AND PARTNERS
P.O. Box 4060
Tel Aviv 61040
ISRAEL

RECEIVED

14-11-2000

REINHOLD COHN & PARTNERS

PCT

WRITTEN OPINION

(PCT Rule 66)

Date of mailing
(day/month/year)

08.11.2000

Applicant's or agent's file reference

121822.1 MM

REPLY DUE

within 2 month(s)
from the above date of mailing

International application No.

PCT/IL99/00681

International filing date (day/month/year)

15/12/1999

Priority date (day/month/year)

15/12/1998

International Patent Classification (IPC) or both national classification and IPC

H01M12/06

Applicant

ELECTRIC FUEL LIMITED et al.

1. This written opinion is the first drawn up by this International Preliminary Examining Authority.

2. This opinion contains indications relating to the following items:

- I ☒ Basis of the opinion
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain document cited
- VII ☐ Certain defects in the international application
- VIII ☒ Certain observations on the international application

3. The applicant is hereby invited to reply to this opinion.

When? See the time limit indicated above. The applicant may, before the expiration of that time limit, request this Authority to grant an extension, see Rule 66.2(d).

How? By submitting a written reply, accompanied, where appropriate, by amendments, according to Rule 66.3. For the form and the language of the amendments, see Rules 66.8 and 66.9.

Also: For an additional opportunity to submit amendments, see Rule 66.4.
For the examiner's obligation to consider amendments and/or arguments, see Rule 66.4 bis.
For an informal communication with the examiner, see Rule 66.8.

If no reply is filed, the international preliminary examination report will be established on the basis of this opinion.

4. The final date by which the international preliminary examination report must be established according to Rule 69.2 is: 15/04/2001.

Name and mailing address of the International preliminary examining authority:

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Authorized officer / Examiner

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International application No. PCT/IL99/00681

1. This opinion has been drawn on the basis of (substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this opinion as "originally filed").

1-17 as originally filed

1-45 as originally filed

1/4-4/4 **as originally filed**

☐ the description, pages:

☐ the claims, Nos.:

☐ the drawings, sheets:

3. This opinion has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

V. Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Novelty (N)	Claims	1, 2, 9, 10, 16, 18, 19, 24, 30, 31, 38, 40	no
Inventive step (IS)	Claims	3-8, 15, 17, 25-29, 39, 41-45	no
Industrial applicability (IA)	Claims		

see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

V.

Novelty.

The present independent claims 1, 16 and 30 are indeterminate in scope in relation to the expression "particles...larger than a predetermined size", to which no definite meaning can be attached unless the "predetermined size" is specified.

The same point also applies to claims 10, 19 and 31 in connection with the expression "a substantial amount of particles with sizes that are close to the predetermined size".

Therefore, such expressions are not regarded as representing true limiting features for the subject-matter of these claims.

The result of this situation is that these claims, in their present wording, are so broad in scope as to embrace subject-matter known from documents cited in the International Search Report.

In this connection, attention is directed to the disclosure of EP-A-0 551 204 (D1) (see e.g. col.4, l.16-19) and the abstract of JP 60 230359 (D2), both relating to metal-air cells having, implicitly or explicitly, substantially all the features of the present cell and in particular an anode (the "mixture" of the present claims) comprising an electrolyte and metal (e.g. Zn) particles.

Each of these disclosures is therefore detrimental to the novelty of the subject-matter of claims 1, 2, 10, 16, 18, 19, 30, 31 and 38.

Moreover, D2 takes away the novelty also of the subject-matter of claims 9, 24 and 40 since it teaches incorporating a gelling agent in the anode mix.

The use of particulate metal anodes in metal-alkaline cells is also known from e.g. the abstracts of JP 60 163367 (D3) and JP 56 145669 (D4).

Inventive step.

Of the remaining claims for which the requisite of novelty can be acknowledged,

those which also would seem to comply with the requirement of inventive step are only those claims which specify the minimum "predetermined size" of the metal particles for which a technical effect has been shown, this in consideration of the data shown in Table 2 and of the passage bridging pp.13 and 14.

An inventive step can therefore be acknowledged to the subject-matter of claims 11, 13, 20, 22, 32 and 35 and of the claims depending therefrom, i.e. claims 12, 14, 21, 23, 33, 34, 36 and 37.

VIII.

1. No technical significance can be attached to the graph of fig.2, since the PEG proportion for each cell A to D is not specified.

Moreover, according to p.14, l.3ff, fig.2 is supposed to show the performance of five cells, but in actual fact fig.2 shows the performance of only four cells.

2. At present p.1, reference is made to unpublished documents.

3. Claims 8 and 17 contain a reference to a trademark.

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January 7, 2001

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OF 16 PAGE(S)
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European Patent Office
D-80298 Munich
Germany

Attention: Del Piero, G. -Examiner
Krage, D. - Formalities Officer

Re: International Application No. PCT/IL99/00681
in the name of Electric Fuel Ltd.
Title: "Corrosion resistant high performance
electrochemical cell"
Your Ref: 248/079PCT
Our Ref: 121822.1-YF

We refer to the Written Opinion of November 8, 2000. In response thereto, please find attached (and enclosed in triplicate with the postal confirmation copy to follow) amended pages 18-22 and newly added page 23. In the amended pages and in the newly added page the following amendments were incorporated:

1. Original claims 1, 8, 16, 17, and 30 were amended.
2. Original claims 11, 13, 20, 22, 32 and 35 were deleted, and three new claims added.

In view of the deletions of claims, remaining claims were renumbered their dependencies amended and thus newly added claims are numbered as 40-42.

In addition we enclose original pages 18-22 with the hand-written amendments incorporated therein.

1. **Claim amendments:**

Original claims 1, 16 and 30, now claims 1, 14 and 26 were amended so as to define the invention and more clearly distinct these independent claims from the prior art. In particular, a phrase defining the particle size was incorporated therein.

Original claims 8 and 17, now claims 8 and 15: the word "Teflon" was substituted by the term "polytetrafluoroethylene-containing compounds".



Newly added independent claims 40-42 recite that the particle-size-selected metal has the feature of a random particle size distribution characteristic of a sieving operation applied to thermal zinc. Such a distribution would be apparent to one of skill in the art, since the normal, unsieved particle size distribution would be well known to such a person, and deviations therefrom likewise would be apparent.

2. Response to the Objections of Lack of Novelty and Lack of Inventive Step

Under section V of the Written Opinion, the Examiner questions the novelty of independent original claims 1, 16 and 30, based on the finding that these claims are indeterminate with respect to the expression "particles...larger than a predetermined size" which originally appeared in these claims. The examiner found that no definite meaning might be applied to these claims unless the predetermined size is specified. The Examiner further found that original claims 10, 19, and 31 are similarly indeterminate with regard to the expression "a substantial amount of particles with sizes that are close to the predetermined size." With regard to these two issues and as indicated above, we have amended original claims 1, 16, and 30 to establish a definite "predetermined size" of not less than about 75 microns.

In addition, also under section V of the Written Opinion, the Examiner questions the inventive step in original claims 1-10, 15-19, 24-31, and 38-45 on the grounds that these claims do not specify a minimum "predetermined size" of the metal particles for which a technical effect has been shown. With regard to these issues, the amendments to independent original claims 1, 16 and 30 include the element of a specified minimum "predetermined size" of the particles for which a technical effect has been shown and considered by the examiner to constitute an inventive step. Thus, independent original claims 1, 16, and 30 should be considered in their present amended wording to constitute an inventive step. Furthermore, the claims dependent on these independent original claims, namely original claims 2-10, 12, 14-19, 21, 23-31, 33, 34, and 36-45.

3. Response to the Comments Re Item VIII

1: The Examiner stated that no technical significance can be attached to Figure 2, since the PEG concentration for each cell is not specified. Applicants note that none of the claims recite a limitation regarding the presence of PEG or its concentration, so the presence or absence of such data, do not impact the present claims.

2: The Examiner stated that Figure 2 shows the performance of four cells, although the specification says the Figure is supposed to show the results of five cells. On the right side of Figure 2, references for cells A-E are shown. The results for cells D and E are very close; thus, although it appears from the

drawing that only four curves are present, in fact there are five curves, two of which (D and E) are virtually identical.

The Examiner is requested to reconsider the objections in light of the submissions made, and a favorable International Preliminary Examination Report (IPER) is requested. However, against the event that the Examiner still has some outstanding objections to the claims, the issuance of a second Written Opinion before the IPER issues is requested.

Yours very truly,
REINHOLD COHN AND PARTNERS
By:


Dr. Yigal Fraenkel

Enc: air mail

AMENDED CLAIM PAGES 18-23

What is claimed is:

1. A metal-alkaline battery cell comprising:
 - a cathode including a catalyst and a conductive material;
 - a first terminal electrically connected to the cathode;
 - 5 a mixture including an electrolyte and particle-size-selected metal, said particle-size-selected metal having a normal distribution wherein an amount of said metal below about 75 microns is less than that predictable from the shape of the particle size distribution curve;
 - a second terminal electronically connected to said mixture; and
 - 10 a separator located between the cathode and the mixture, in physical contact with the cathode and with the mixture, said separator being of such material as to permit ions to travel between the cathode and the mixture and to block metal particles from contacting the cathode.
- 15 2. The battery cell of claim 1, wherein the particle-size-selected metal includes particle-size-selected zinc.
3. The battery cell of claim 2, wherein the particle-size-selected zinc accounts for about 60% of the mixture by weight.
- 20 4. The battery cell of claim 2, wherein the mixture includes electrolytic zinc.
5. The battery cell of claim 4, wherein a ratio of electrolytic zinc to particle-size-selected zinc in the mixture is between about 1:9 and about 1:1.
- 25 6. The battery cell of claim 4, wherein the electrolytic zinc and the particle-size-selected zinc, taken together, account for about 60% of the mixture by weight.
7. The battery cell of claim 1, wherein the conductive material includes carbon.
8. The battery cell of claim 1, wherein the separator includes a
30 polytetrafluoroethylene-containing compound.
9. The battery cell of claim 1, wherein the mixture includes a gelling agent.

10. The battery cell of claim 1, wherein the particle-size-selected metal contains a substantial amount of particles with sizes that are close to the predetermined size.

11. The battery cell of claim 10, wherein substantially all particles contained in the particle-size-selected metal are smaller than about 500 microns.

12. The battery cell of claim 10, wherein substantially all particles contained in the particle-size-selected metal are smaller than about 500 microns.

13. The battery cell of claim 1, wherein a corrosion-inhibiting agent is alloyed in the particle-size-selected metal.

14. A metal-air battery cell comprising:

an air electrode;

a first terminal electrically connected to the air electrode;

a mixture including an electrolyte and particle-size-selected metal, said particle size-selected metal having a normal distribution wherein an amount of said metal below about 75 microns is less than that predictable from the shape of the particle size distribution curve;

a second terminal electronically connected to said mixture; and

a separator located between the air electrode and the mixture, in physical contact with the air electrode and with the mixture, said separator being of such material as to permit ions to travel between the air electrode and the mixture and to block metal particles from contacting the air electrode.

15. The battery cell of claim 14, wherein the separator includes a polytetrafluoroethylene-containing compound.

16. The battery cell of claim 14, wherein the particle-size-selected metal includes particle-size-selected zinc.

17. The battery cell of claim 16, wherein the particle-size-selected zinc contains a substantial amount of particles with sizes that are close to the predetermined size.

18. The battery cell of claim 17, wherein substantially all particles contained in the particle-size-selected zinc are smaller than about 500 microns.

19. The battery cell of claim 18, wherein substantially all particles contained in the particle-size-selected zinc are smaller than about 500 microns.

20. The battery cell of claim 17, wherein the mixture includes a gelling agent.

21. The battery cell of claim 17, wherein a corrosion-inhibiting agent is alloyed in the particle-size-selected zinc.

22. The battery cell of claim 17, wherein the particle-size-selected zinc accounts for about 60% of the mixture by weight.

23. The battery cell of claim 17, wherein the mixture includes electrolytic zinc.

24. The battery cell of claim 23, wherein a ratio of electrolytic zinc to particle-size-selected zinc in the mixture is between about 1:9 and about 1:1.

25. The battery cell of claim 23, wherein the electrolytic zinc and the particle-size-selected zinc, taken together, account for about 60% of the mixture by weight.

26. A method of forming a corrosion resistant metal-air battery cell comprising the steps of:

forming a mixture by mixing ingredients including an electrolyte and particle-size-selected metal, said particle size-selected metal having a normal distribution wherein an amount of said metal below about 75 microns is less than that predictable from the shape of the particle size distribution curve;

electrically connecting a first terminal to the mixture obtained in the forming step;

obtaining an air electrode with a second terminal connected thereto; and positioning a separator between the air electrode and the mixture, in physical contact with the air electrode and with the mixture, wherein the separator permits ions to travel between the air electrode and the mixture and blocks metal particles from contacting the air electrode.

27. The method of claim 26, wherein the particle-size-selected metal contains a substantial amount of particles with sizes that are close to the predetermined size.

23. The method of claim 27, wherein the particle-size-selected metal includes particle-size-selected zinc.

29. The method of claim 27, wherein substantially all particles contained in the particle-size-selected metal are smaller than about 500 microns.

30. The method of claim 27, wherein the particle-size-selected metal includes particle-size-selected zinc.

31. The method of claim 27, wherein substantially all particles contained in the particle-size-selected metal are smaller than about 500 microns.

32. The method of claim 27, wherein the particle-size-selected metal is obtained by removing substantially all metal particles that are smaller than the predetermined size from a batch of metal particles.

33. The method of claim 32, wherein a sieve is used to remove substantially all of the metal particles that are smaller than the predetermined size.

34. The method of claim 27, wherein the mixture formed in the forming step includes a gelling agent.

35. The method of claim 27, wherein a corrosion-inhibiting agent is alloyed in the particle-size-selected metal.

36. The method of claim 27, wherein the particle-size-selected metal includes particle-

size-selected zinc, and the particle-size-selected zinc accounts about 60% by weight of the mixture formed in the forming step.

37. The method of claim 27, wherein the particle-size-selected metal includes particle-size-selected zinc, and the mixture formed in the forming step includes electrolytic zinc.

38. The method of claim 37, wherein a ratio of electrolytic zinc to particle-size-selected zinc in the mixture formed in the forming step is between about 1:9 and about 1:1.

39. The method of claim 37, wherein the electrolytic zinc and the particle-size-selected zinc, taken together, account for about 60% by weight of the mixture formed in the forming

40. A metal-alkaline battery cell comprising:

a cathode including a catalyst and a conductive material;

a first terminal electrically connected to the cathode;

an anode mixture including an electrolyte and thermal zinc, said thermal zinc having a normal particle size distribution characteristic of thermal generation of said thermal zinc except for a precipitous truncation of said normal particle distribution such as would result from a sieving operation applied to thermal zinc;

a second terminal electronically connected to said mixture; and

a separator located between the cathode and the mixture, in physical contact with the cathode and with the mixture, said separator being of such material as to permit ions to travel between the cathode and the mixture and to block metal particles from contacting the cathode.

41. A metal-air battery cell comprising:

an air electrode;

a first terminal electrically connected to the air electrode;

an anode mixture including an electrolyte and thermal zinc, said thermal zinc having a characteristic of thermal generation of said thermal zinc except for a precipitous truncation of said particle-size-selected material, said particle-size-selected material having a random particle size distribution characteristic of a sieving operation applied to thermal zinc, such as would result from a sieving operation applied to said thermal zinc;

a second terminal electronically connected to said mixture; and
a separator located between the air electrode and the mixture, in physical
contact with the air electrode and with the mixture, said separator being of such
material as to permit ions to travel between the air electrode and the mixture and to
5 block metal particles from contacting the air electrode.

42. A method of forming a corrosion resistant metal-air battery cell comprising
the steps of:

10 forming an anode mixture by mixing ingredients including an electrolyte and
thermal zinc, said thermal zinc having a normal particle size distribution characteristic
of thermal generation of said thermal zinc except for a precipitous truncation of said
normal particle size distribution, such as would result from a sieving operation
applied to thermal zinc;

15 electrically connecting a first terminal to the anode mixture obtained in the
forming step;

obtaining an air electrode with a second terminal connected thereto; and

positioning a separator between the air electrode and the anode mixture, in physical
contact with the air electrode and with the anode mixture, wherein the separator permits
ions to travel between the air electrode and the anode mixture and blocks metal particles
20 from contacting the air electrode.

ORIGINAL CLAIM PAGES 18-22 WITH
HANDWRITTEN AMENDMENTS

What is claimed is:

*said metal below about 75 microns is less than
that predictable from the shape of the particle size
distribution curve >*

1. A metal-alkaline battery cell comprising:
 - a cathode including a catalyst and a conductive material;
 - 5 a first terminal electrically connected to the cathode;
 - a mixture including an electrolyte and particle-size-selected metal;
 - <A> →* a second terminal electrically connected to the mixture; and
 - a separator located between the cathode and the mixture, in physical contact with the cathode and with the mixture, said separator being of such material as to permit ions to travel
 - 10 between the cathode and the mixture and to block metal particles from contacting the cathode_x.
 - ~~wherein substantially all particles contained in the particle-size-selected metal are larger than a predetermined size.~~
2. The battery cell of claim 1, wherein the wherein the particle-size-selected metal
- 15 includes particle-size-selected zinc.
3. The battery cell of claim 2, wherein the particle-size-selected zinc accounts for about 60% of the mixture by weight.
- 20 4. The battery cell of claim 2, wherein the mixture includes electrolytic zinc.
5. The battery cell of claim 4, wherein a ratio of electrolytic zinc to particle-size-selected zinc in the mixture is between about 1:9 and about 1:1.
- 25 6. The battery cell of claim 4, wherein the electrolytic zinc and the particle-size-selected zinc, taken together, account for about 60% of the mixture by weight.
7. The battery cell of claim 1, wherein the conductive material includes carbon.
- 30 8. The battery cell of claim 1, wherein the wherein the separator includes Teflon_x a polytetrafluoroethylene-containing compound.
9. The battery cell of claim 1, wherein the mixture includes a gelling agent.

10. The battery cell of claim 1, wherein the particle-size-selected metal contains a substantial amount of particles with sizes that are close to the predetermined size.

~~11. The battery cell of claim 10, wherein the predetermined size is about 75 microns.~~

5
11 12. The battery cell of claim ¹⁰11, wherein substantially all particles contained in the particle-size-selected metal are smaller than about 500 microns.

~~13. The battery cell of claim 10, wherein the predetermined size is about 100 microns.~~

10
12 14. The battery cell of claim ¹⁰13, wherein substantially all particles contained in the particle-size-selected metal are smaller than about 500 microns.

13 15. The battery cell of claim 1, wherein a corrosion-inhibiting agent is alloyed in the
15 particle-size-selected metal.

14 16. A metal-air battery cell comprising:
an air electrode;
a first terminal electrically connected to the air electrode;
20 a mixture including an electrolyte and particle-size-selected metal;
< A > —> a second terminal electrically connected to the mixture; and
a separator located between the air electrode and the mixture, in physical contact with
the air electrode and with the mixture, said separator being of such material as to permit ions
to travel between the air electrode and the mixture and to block metal particles from
25 contacting the air electrode.

~~wherein substantially all particles contained in the particle-size-selected metal are
larger than a predetermined size.~~

15 17. The battery cell of claim ¹⁴16, wherein ~~the wherein~~ the separator includes Teflon,
30 a polytetrafluoroethylene-containing compound

16 18. The battery cell of claim ¹⁴16, wherein the particle-size-selected metal includes particle-size-selected zinc.

~~19.~~ The battery cell of claim ¹⁸, wherein the particle-size-selected zinc contains a substantial amount of particles with sizes that are close to the predetermined size.

~~20.~~ The battery cell of claim ~~19~~, wherein the predetermined size is about 75 microns. /

5

¹⁷
18 ~~21.~~ The battery cell of claim ²⁰, wherein substantially all particles contained in the particle-size-selected zinc are smaller than about 500 microns.

~~22.~~ The battery cell of claim ~~19~~, wherein the predetermined size is about 100 microns. /

10

¹⁸
~~23.~~ The battery cell of claim ²², wherein substantially all particles contained in the particle-size-selected zinc are smaller than about 500 microns.

¹⁷
~~24.~~ The battery cell of claim ~~19~~, wherein the mixture includes a gelling agent.

15

¹⁷
~~25.~~ The battery cell of claim ~~19~~, wherein a corrosion-inhibiting agent is alloyed in the particle-size-selected zinc.

¹²
~~26.~~ The battery cell of claim ~~19~~, wherein the particle-size-selected zinc accounts for about 60% of the mixture by weight.

¹⁷
~~27.~~ The battery cell of claim ~~19~~, wherein the mixture includes electrolytic zinc.

²³
~~28.~~ The battery cell of claim ²⁷, wherein a ratio of electrolytic zinc to particle-size-selected zinc in the mixture is between about 1:9 and about 1:1.

²³
~~29.~~ The battery cell of claim ²⁷, wherein the electrolytic zinc and the particle-size-selected zinc, taken together, account for about 60% of the mixture by weight.

²⁶
~~30.~~ A method of forming a corrosion resistant metal-air battery cell comprising the steps of:

forming a mixture by mixing ingredients including an electrolyte and particle-size-selected metal;

electrically connecting a first terminal to the mixture obtained in the forming step;
obtaining an air electrode with a second terminal connected thereto; and

positioning a separator between the air electrode and the mixture, in physical contact
with the air electrode and with the mixture, wherein the separator permits ions to travel
5 between the air electrode and the mixture and blocks metal particles from contacting the air
electrode.

~~/wherein substantially all particles contained in the particle-size-selected zinc are larger
than a predetermined size/~~

10 ²⁷ 31. The method of claim ²⁶ 30, wherein the particle-size-selected metal contains a substantial
amount of particles with sizes that are close to the predetermined size.

~~32. The method of claim 31, wherein the predetermined size is about 75 microns.~~

15 ²⁷ 33. The method of claim ²⁷ 32, wherein the particle-size-selected metal includes particle-
size-selected zinc.

²⁹ 34. The method of claim ²⁷ 32, wherein substantially all particles contained in the particle-
size-selected metal are smaller than about 500 microns.

20

~~35. The method of claim 31, wherein the predetermined size is about 100 microns.)~~

²⁷ 36. The method of claim ²⁷ 35, wherein the particle-size-selected metal includes particle-
size-selected zinc.

25

²⁷ 37. The method of claim ²⁷ 36, wherein substantially all particles contained in the particle-
size-selected metal are smaller than about 500 microns.

³² 38. The method of claim ²⁷ 31, wherein the particle-size-selected metal is obtained by
30 removing substantially all metal particles that are smaller than the predetermined size from a
batch of metal particles.

³² 39. The method of claim ³² 38, wherein a sieve is used to remove substantially all of the

metal particles that are smaller than the predetermined size.

34 40. The method of claim ²⁷31, wherein the mixture formed in the forming step includes a gelling agent.

5 35 41. The method of claim ²⁷31, wherein a corrosion-inhibiting agent is alloyed in the particle-size-selected metal.

36 42. The method of claim ²⁷31, wherein the particle-size-selected metal includes particle-size-selected zinc, and the particle-size-selected zinc accounts for about 60% by weight of the mixture formed in the forming step.

37 43. The method of claim ²⁷31, wherein the particle-size-selected metal includes particle-size-selected zinc, and the mixture formed in the forming step includes electrolytic zinc.

15 38 44. The method of claim ³²43, wherein a ratio of electrolytic zinc to particle-size-selected zinc in the mixture formed in the forming step is between about 1:9 and about 1:1.

39 45. The method of claim ³²43, wherein the electrolytic zinc and the particle-size-selected zinc, taken together, account for about 60% by weight of the mixture formed in the forming step.

PATENT COOPERATION TREATY

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 121822.1 MM	<div style="display: flex; justify-content: space-between;"> <div> FOR FURTHER ACTION </div> <div> <small>See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)</small> </div> </div>	
International application No. PCT/IL99/00681	International filing date (<i>day/month/year</i>) 15/12/1999	Priority date (<i>day/month/year</i>) 15/12/1998
International Patent Classification (IPC) or national classification and IPC H01M12/06		
Applicant ELECTRIC FUEL LIMITED et al.		

1.	This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2.	This REPORT consists of a total of 6 sheets, including this cover sheet. <input checked="" type="checkbox"/> This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT). These annexes consist of a total of 6 sheets.

3.	This report contains indications relating to the following items: <ul style="list-style-type: none"> I <input checked="" type="checkbox"/> Basis of the report II <input type="checkbox"/> Priority III <input checked="" type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability IV <input type="checkbox"/> Lack of unity of invention V <input type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement VI <input type="checkbox"/> Certain documents cited VII <input type="checkbox"/> Certain defects in the international application VIII <input type="checkbox"/> Certain observations on the international application
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Date of submission of the demand 03/07/2000	Date of completion of this report 06.04.2001
Name and mailing address of the international preliminary examining authority: <div style="display: flex; align-items: center;"> <div> European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d </div> </div>	Authorized officer Del Piero, G



INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/IL99/00681

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, pages:

1-17 as originally filed

Claims, No.:

1-42 with telefax of 07/01/2001

Drawings, sheets:

1/4-4/4 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/IL99/00681

☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

III. Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

1. The questions whether the claimed invention appears to be novel, to involve an inventive step (to be non-obvious), or to be industrially applicable have not been examined in respect of:

☐ the entire international application.

☒ claims Nos. 1, 14, 26, 40, 41, 42.

because:

☐ the said international application, or the said claims Nos. relate to the following subject matter which does not require an international preliminary examination (*specify*):

☐ the description, claims or drawings (*indicate particular elements below*) or said claims Nos. are so unclear that no meaningful opinion could be formed (*specify*):

☒ the claims, or said claims Nos. 1, 14, 26, 40, 41 42 (see Sep.Sheet). are so inadequately supported by the description that no meaningful opinion could be formed.

☐ no international search report has been established for the said claims Nos. .

2. A meaningful international preliminary examination cannot be carried out due to the failure of the nucleotide and/or amino acid sequence listing to comply with the standard provided for in Annex C of the Administrative Instructions:

☐ the written form has not been furnished or does not comply with the standard.

☐ the computer readable form has not been furnished or does not comply with the standard.

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/IL99/00681

III.

The current set of claims does not comply with the provisions of Art.34(2)(b) in that the present amendments go beyond the disclosure of the international application as filed.

In particular, independent claims 1, 14 and 26 rely on the expression "... said particle-size-selected metal having a normal distribution wherein an amount of said metal below about 75 microns is less than that predictable from the shape of the particle size distribution curve ..." for which there is no basis in the application as originally filed.

The same point applies to independent claims 40, 41 and 42 with respect to the expression "... said thermal zinc having a normal particle size distribution characteristic of thermal generation of said thermal zinc except for a precipitous truncation of said normal particle distribution such as would result from a sieving operation applied to thermal zinc ...".

In this connection, the only mention in the original specification of a sieving operation is in the context of a particular thermal zinc (Mitsui) with a specific particle size limit (75 micrometres), see p.12, l.21 to p.13, l.2.

Therefore, this passage does not provide sufficient support for the generalisation implied by the amended wording of claims 40, 41 and 42.

The consequence of this is that no assessment can be made as to whether the subject-matter of the current claims, including the subordinate claims, complies with the requirements of novelty and inventive step having regard to the available state of the art.

However, for the Applicant's benefit, the following points are noted with respect to the claims as originally filed, i.e. as if the amendments referred to in section III. had not been effected.

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/IL99/00681

Novelty.

The independent claims 1, 16 and 30 are indeterminate in scope in relation to the expression "particles...larger than a predetermined size", to which no definite meaning can be attached unless the "predetermined size" is specified.

The same point also applies to claims 10, 19 and 31 in connection with the expression "a substantial amount of particles with sizes that are close to the predetermined size".

Therefore, such expressions are not regarded as representing true limiting features for the subject-matter of these claims.

The result of this situation is that these claims, in their present wording, are so broad in scope as to embrace subject-matter known from documents cited in the International Search Report.

In this connection, attention is directed to the disclosure of EP-A-0 551 204 (D1) (see e.g. col.4, l.16-19) and the abstract of JP 60 230359 (D2), both relating to metal-air cells having, implicitly or explicitly, substantially all the features of the present cell and in particular an anode (the "mixture" of the present claims) comprising an electrolyte and metal (e.g. Zn) particles.

Each of these disclosures is therefore detrimental to the novelty of the subject-matter of claims 1, 2, 10, 16, 18, 19, 30, 31 and 38.

Moreover, D2 takes away the novelty also of the subject-matter of claims 9, 24 and 40 since it teaches incorporating a gelling agent in the anode mix.

The use of particulate metal anodes in metal-alkaline cells is also known from e.g. the abstracts of JP 60 163367 (D3) and JP 56 145669 (D4).

Inventive step.

Of the remaining claims for which the requisite of novelty can be acknowledged, those which also would seem to comply with the requirement of inventive step are only those claims which specify the minimum "predetermined size" of the metal particles for which a technical effect has been shown, this in consideration of the data shown in

INTERNATIONAL PRELIMINARY

International application No. PCT/IL99/00681

EXAMINATION REPORT - SEPARATE SHEET

Table 2 and of the passage bridging pp.13 and 14.

An inventive step can therefore be acknowledged to the subject-matter of claims 11, 13, 20, 22, 32 and 35 and of the claims depending therefrom, i.e. claims 12, 14, 21, 23, 33, 34, 36 and 37.

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What is claimed is:

1. A metal-alkaline battery cell comprising:
 - a cathode including a catalyst and a conductive material;
 - a first terminal electrically connected to the cathode;
 - 5 a mixture including an electrolyte and particle-size-selected metal, said particle-size-selected metal having a normal distribution wherein an amount of said metal below about 75 microns is less than that predictable from the shape of the particle size distribution curve;
 - a second terminal electronically connected to said mixture; and
 - 10 a separator located between the cathode and the mixture, in physical contact with the cathode and with the mixture, said separator being of such material as to permit ions to travel between the cathode and the mixture and to block metal particles from contacting the cathode.
- 15 2. The battery cell of claim 1, wherein the wherein the particle-size-selected metal includes particle-size-selected zinc.
3. The battery cell of claim 2, wherein the particle-size-selected zinc accounts for about 60% of the mixture by weight.
- 20 4. The battery cell of claim 2, wherein the mixture includes electrolytic zinc.
5. The battery cell of claim 4, wherein a ratio of electrolytic zinc to particle-size-selected zinc in the mixture is between about 1:9 and about 1:1.
- 25 6. The battery cell of claim 4, wherein the electrolytic zinc and the particle-size-selected zinc, taken together, account for about 60% of the mixture by weight.
7. The battery cell of claim 1, wherein the conductive material includes carbon.
8. The battery cell of claim 1, wherein the separator includes a
30 polytetrafluoroethylene-containing compound.
9. The battery cell of claim 1, wherein the mixture includes a gelling agent.

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10. The battery cell of claim 1, wherein the particle-size-selected metal contains a substantial amount of particles with sizes that are close to the predetermined size.

11. The battery cell of claim 10, wherein substantially all particles contained in the particle-size-selected metal are smaller than about 500 microns.

12. The battery cell of claim 10, wherein substantially all particles contained in the particle-size-selected metal are smaller than about 500 microns.

13. The battery cell of claim 1, wherein a corrosion-inhibiting agent is alloyed in the particle-size-selected metal.

14. A metal-air battery cell comprising:

an air electrode;

a first terminal electrically connected to the air electrode;

a mixture including an electrolyte and particle-size-selected metal, said particle size-selected metal having a normal distribution wherein an amount of said metal below about 75 microns is less than that predictable from the shape of the particle size distribution curve;

a second terminal electronically connected to said mixture; and

a separator located between the air electrode and the mixture, in physical contact with the air electrode and with the mixture, said separator being of such material as to permit ions to travel between the air electrode and the mixture and to block metal particles from contacting the air electrode.

15. The battery cell of claim 14, wherein the separator includes a polytetrafluoroethylene-containing compound.

16. The battery cell of claim 14, wherein the particle-size-selected metal includes particle-size-selected zinc.

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17. The battery cell of claim 16, wherein the particle-size-selected zinc contains a substantial amount of particles with sizes that are close to the predetermined size.

18. The battery cell of claim 17, wherein substantially all particles contained in the particle-size-selected zinc are smaller than about 500 microns.

19. The battery cell of claim 18, wherein substantially all particles contained in the particle-size-selected zinc are smaller than about 500 microns.

20. The battery cell of claim 17, wherein the mixture includes a gelling agent.

21. The battery cell of claim 17, wherein a corrosion-inhibiting agent is alloyed in the particle-size-selected zinc.

22. The battery cell of claim 17, wherein the particle-size-selected zinc accounts for about 60% of the mixture by weight.

23. The battery cell of claim 17, wherein the mixture includes electrolytic zinc.

24. The battery cell of claim 23, wherein a ratio of electrolytic zinc to particle-size-selected zinc in the mixture is between about 1:9 and about 1:1.

25. The battery cell of claim 23, wherein the electrolytic zinc and the particle-size-selected zinc, taken together, account for about 60% of the mixture by weight.

26. A method of forming a corrosion resistant metal-air battery cell comprising the steps of:

forming a mixture by mixing ingredients including an electrolyte and particle-size-selected metal, said particle size-selected metal having a normal distribution wherein an amount of said metal below about 75 microns is less than that predictable from the shape of the particle size distribution curve;

electrically connecting a first terminal to the mixture obtained in the forming

step;

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obtaining an air electrode with a second terminal connected thereto; and
positioning a separator between the air electrode and the mixture, in physical
contact with the air electrode and with the mixture, wherein the separator permits ions
to travel between the air electrode and the mixture and blocks metal particles from
contacting the air electrode.

27. The method of claim 26, wherein the particle-size-selected metal contains a substantial
amount of particles with sizes that are close to the predetermined size.

28. The method of claim 27, wherein the particle-size-selected metal includes particle-
size-selected zinc.

29. The method of claim 27, wherein substantially all particles contained in the particle-
size-selected metal are smaller than about 500 microns.

30. The method of claim 27, wherein the particle-size-selected metal includes particle-
size-selected zinc.

31. The method of claim 27, wherein substantially all particles contained in the particle-
size-selected metal are smaller than about 500 microns.

32. The method of claim 27, wherein the particle-size-selected metal is obtained by
removing substantially all metal particles that are smaller than the predetermined size from a
batch of metal particles.

33. The method of claim 32, wherein a sieve is used to remove substantially all of the
metal particles that are smaller than the predetermined size.

34. The method of claim 27, wherein the mixture formed in the forming step includes a
gelling agent.

35. The method of claim 27, wherein a corrosion-inhibiting agent is alloyed in the
particle-size-selected metal.

36. The method of claim 27, wherein the particle-size-selected metal includes particle-

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size-selected zinc, and the particle-size-selected zinc accounts for about 60% by weight of the mixture formed in the forming step.

37. The method of claim 27, wherein the particle-size-selected metal includes particle-size-selected zinc, and the mixture formed in the forming step includes electrolytic zinc.

38. The method of claim 37, wherein a ratio of electrolytic zinc to particle-size-selected zinc in the mixture formed in the forming step is between about 1:9 and about 1:1.

39. The method of claim 37, wherein the electrolytic zinc and the particle-size-selected zinc, taken together, account for about 60% by weight of the mixture formed in the forming

40. A metal-alkaline battery cell comprising:

a cathode including a catalyst and a conductive material;

a first terminal electrically connected to the cathode;

an anode mixture including an electrolyte and thermal zinc, said thermal zinc having a normal particle size distribution characteristic of thermal generation of said thermal zinc except for a precipitous truncation of said normal particle distribution such as would result from a sieving operation applied to thermal zinc;

a second terminal electronically connected to said mixture; and

a separator located between the cathode and the mixture, in physical contact with the cathode and with the mixture, said separator being of such material as to permit ions to travel between the cathode and the mixture and to block metal particles from contacting the cathode.

41. A metal-air battery cell comprising:

an air electrode;

a first terminal electrically connected to the air electrode;

an anode mixture including an electrolyte and thermal zinc, said thermal zinc having a characteristic of thermal generation of said thermal zinc except for a precipitous truncation of said particle-size-selected material, said particle-size-selected material having a random particle size distribution characteristic of a sieving operation applied to thermal zinc, such as would result from a sieving operation applied to said thermal zinc;

PATENT COOPERATION TREATY

PCT

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 121822.1 MM	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/IL99/00681	International filing date (day/month/year) 15/12/1999	Priority date (day/month/year) 15/12/1998
International Patent Classification (IPC) or national classification and IPC H01M12/06		
Applicant ELECTRIC FUEL LIMITED et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.



2. This REPORT consists of a total of 6 sheets, including this cover sheet.

- ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 6 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☒ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☐ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

Date of submission of the demand 03/07/2000	Date of completion of this report 06.04.2001
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Del Piero, G Telephone No. +49 89 2399 8579 

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/IL99/00681

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, pages:

1-17 as originally filed

Claims, No.:

1-42 with telefax of 07/01/2001

Drawings, sheets:

1/4-4/4 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/IL99/00681

☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

III. Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

1. The questions whether the claimed invention appears to be novel, to involve an inventive step (to be non-obvious), or to be industrially applicable have not been examined in respect of:

☐ the entire international application.

☒ claims Nos. 1, 14, 26, 40, 41, 42.

because:

☐ the said international application, or the said claims Nos. relate to the following subject matter which does not require an international preliminary examination (*specify*):

☐ the description, claims or drawings (*indicate particular elements below*) or said claims Nos. are so unclear that no meaningful opinion could be formed (*specify*):

☒ the claims, or said claims Nos. 1, 14, 26, 40, 41 42 (see Sep.Sheet). are so inadequately supported by the description that no meaningful opinion could be formed.

☐ no international search report has been established for the said claims Nos. .

2. A meaningful international preliminary examination cannot be carried out due to the failure of the nucleotide and/or amino acid sequence listing to comply with the standard provided for in Annex C of the Administrative Instructions:

☐ the written form has not been furnished or does not comply with the standard.

☐ the computer readable form has not been furnished or does not comply with the standard.

III.

The current set of claims does not comply with the provisions of Art.34(2)(b) in that the present amendments go beyond the disclosure of the international application as filed.

In particular, independent claims 1, 14 and 26 rely on the expression "... said particle-size-selected metal having a normal distribution wherein an amount of said metal below about 75 microns is less than that predictable from the shape of the particle size distribution curve ..." for which there is no basis in the application as originally filed.

The same point applies to independent claims 40, 41 and 42 with respect to the expression "... said thermal zinc having a normal particle size distribution characteristic of thermal generation of said thermal zinc except for a precipitous truncation of said normal particle distribution such as would result from a sieving operation applied to thermal zinc ...".

In this connection, the only mention in the original specification of a sieving operation is in the context of a particular thermal zinc (Mitsui) with a specific particle size limit (75 micrometres), see p.12, l.21 to p.13, l.2.

Therefore, this passage does not provide sufficient support for the generalisation implied by the amended wording of claims 40, 41 and 42.

The consequence of this is that no assessment can be made as to whether the subject-matter of the current claims, including the subordinate claims, complies with the requirements of novelty and inventive step having regard to the available state of the art.

However, for the Applicant's benefit, the following points are noted with respect to the claims as originally filed, i.e. as if the amendments referred to in section III. had not been effected.

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Novelty.

The independent claims 1, 16 and 30 are indeterminate in scope in relation to the expression "particles...larger than a predetermined size", to which no definite meaning can be attached unless the "predetermined size" is specified.

The same point also applies to claims 10, 19 and 31 in connection with the expression "a substantial amount of particles with sizes that are close to the predetermined size".

Therefore, such expressions are not regarded as representing true limiting features for the subject-matter of these claims.

The result of this situation is that these claims, in their present wording, are so broad in scope as to embrace subject-matter known from documents cited in the International Search Report.

In this connection, attention is directed to the disclosure of EP-A-0 551 204 (D1) (see e.g. col.4, l.16-19) and the abstract of JP 60 230359 (D2), both relating to metal-air cells having, implicitly or explicitly, substantially all the features of the present cell and in particular an anode (the "mixture" of the present claims) comprising an electrolyte and metal (e.g. Zn) particles.

Each of these disclosures is therefore detrimental to the novelty of the subject-matter of claims 1, 2, 10, 16, 18, 19, 30, 31 and 38.

Moreover, D2 takes away the novelty also of the subject-matter of claims 9, 24 and 40 since it teaches incorporating a gelling agent in the anode mix.

The use of particulate metal anodes in metal-alkaline cells is also known from e.g. the abstracts of JP 60 163367 (D3) and JP 56 145669 (D4).

Inventive step.

Of the remaining claims for which the requisite of novelty can be acknowledged, those which also would seem to comply with the requirement of inventive step are only those claims which specify the minimum "predetermined size" of the metal particles for which a technical effect has been shown, this in consideration of the data shown in

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Table 2 and of the passage bridging pp.13 and 14.

An inventive step can therefore be acknowledged to the subject-matter of claims 11, 13, 20, 22, 32 and 35 and of the claims depending therefrom, i.e. claims 12, 14, 21, 23, 33, 34, 36 and 37.

What is claimed is:

1. A metal-alkaline battery cell comprising:
a cathode including a catalyst and a conductive material;
5 a first terminal electrically connected to the cathode;
a mixture including an electrolyte and particle-size-selected metal;
a second terminal electrically connected to the mixture; and
a separator located between the cathode and the mixture, in physical contact with the
cathode and with the mixture, said separator being of such material as to permit ions to travel
10 between the cathode and the mixture and to block metal particles from contacting the cathode,
wherein substantially all particles contained in the particle-size-selected metal are
larger than a predetermined size.
2. The battery cell of claim 1, wherein the wherein the particle-size-selected metal
15 includes particle-size-selected zinc.
3. The battery cell of claim 2, wherein the particle-size-selected zinc accounts for about
60% of the mixture by weight.
- 20 4. The battery cell of claim 2, wherein the mixture includes electrolytic zinc.
5. The battery cell of claim 4, wherein a ratio of electrolytic zinc to particle-size-selected
zinc in the mixture is between about 1:9 and about 1:1.
- 25 6. The battery cell of claim 4, wherein the electrolytic zinc and the particle-size-selected
zinc, taken together, account for about 60% of the mixture by weight.
7. The battery cell of claim 1, wherein the conductive material includes carbon.
- 30 8. The battery cell of claim 1, wherein the wherein the separator includes Teflon.
9. The battery cell of claim 1, wherein the mixture includes a gelling agent.

10. The battery cell of claim 1, wherein the particle-size-selected metal contains a substantial amount of particles with sizes that are close to the predetermined size.
11. The battery cell of claim 10, wherein the predetermined size is about 75 microns.
- 5 12. The battery cell of claim 11, wherein substantially all particles contained in the particle-size-selected metal are smaller than about 500 microns.
13. The battery cell of claim 10, wherein the predetermined size is about 100 microns.
- 10 14. The battery cell of claim 13, wherein substantially all particles contained in the particle-size-selected metal are smaller than about 500 microns.
- 15 15. The battery cell of claim 1, wherein a corrosion-inhibiting agent is alloyed in the particle-size-selected metal.
16. A metal-air battery cell comprising:
an air electrode;
a first terminal electrically connected to the air electrode;
20 a mixture including an electrolyte and particle-size-selected metal;
a second terminal electrically connected to the mixture; and
a separator located between the air electrode and the mixture, in physical contact with the air electrode and with the mixture, said separator being of such material as to permit ions to travel between the air electrode and the mixture and to block metal particles from
25 contacting the air electrode,
wherein substantially all particles contained in the particle-size-selected metal are larger than a predetermined size.
17. The battery cell of claim 16, wherein the separator includes Teflon.
- 30 18. The battery cell of claim 16, wherein the particle-size-selected metal includes particle-size-selected zinc.

19. The battery cell of claim 18, wherein the particle-size-selected zinc contains a substantial amount of particles with sizes that are close to the predetermined size.
20. The battery cell of claim 19, wherein the predetermined size is about 75 microns.
- 5 21. The battery cell of claim 20, wherein substantially all particles contained in the particle-size-selected zinc are smaller than about 500 microns.
22. The battery cell of claim 19, wherein the predetermined size is about 100 microns.
- 10 23. The battery cell of claim 22, wherein substantially all particles contained in the particle-size-selected zinc are smaller than about 500 microns.
24. The battery cell of claim 19, wherein the mixture includes a gelling agent.
- 15 25. The battery cell of claim 19, wherein a corrosion-inhibiting agent is alloyed in the particle-size-selected zinc.
26. The battery cell of claim 19, wherein the particle-size-selected zinc accounts for about
- 20 60% of the mixture by weight.
27. The battery cell of claim 19, wherein the mixture includes electrolytic zinc.
28. The battery cell of claim 27, wherein a ratio of electrolytic zinc to particle-size-
- 25 selected zinc in the mixture is between about 1:9 and about 1:1.
29. The battery cell of claim 27, wherein the electrolytic zinc and the particle-size-selected zinc, taken together, account for about 60% of the mixture by weight.
- 30 30. A method of forming a corrosion resistant metal-air battery cell comprising the steps of:
- forming a mixture by mixing ingredients including an electrolyte and particle-size-selected metal;

electrically connecting a first terminal to the mixture obtained in the forming step;
obtaining an air electrode with a second terminal connected thereto; and
positioning a separator between the air electrode and the mixture, in physical contact
with the air electrode and with the mixture, wherein the separator permits ions to travel
5 between the air electrode and the mixture and blocks metal particles from contacting the air
electrode,

wherein substantially all particles contained in the particle-size-selected zinc are larger
than a predetermined size.

10 31. The method of claim 30, wherein the particle-size-selected metal contains a substantial
amount of particles with sizes that are close to the predetermined size.

32. The method of claim 31, wherein the predetermined size is about 75 microns.

15 33. The method of claim 32, wherein the particle-size-selected metal includes particle-
size-selected zinc.

34. The method of claim 32, wherein substantially all particles contained in the particle-
size-selected metal are smaller than about 500 microns.

20

35. The method of claim 31, wherein the predetermined size is about 100 microns.

36. The method of claim 35, wherein the particle-size-selected metal includes particle-
size-selected zinc.

25

37. The method of claim 35, wherein substantially all particles contained in the particle-
size-selected metal are smaller than about 500 microns.

38. The method of claim 31, wherein the particle-size-selected metal is obtained by
30 removing substantially all metal particles that are smaller than the predetermined size from a
batch of metal particles.

39. The method of claim 38, wherein a sieve is used to remove substantially all of the

metal particles that are smaller than the predetermined size.

40. The method of claim 31, wherein the mixture formed in the forming step includes a gelling agent.

5

41. The method of claim 31, wherein a corrosion-inhibiting agent is alloyed in the particle-size-selected metal.

42. The method of claim 31, wherein the particle-size-selected metal includes particle-size-selected zinc, and the particle-size-selected zinc accounts for about 60% by weight of the mixture formed in the forming step.

10

43. The method of claim 31, wherein the particle-size-selected metal includes particle-size-selected zinc, and the mixture formed in the forming step includes electrolytic zinc.

15

44. The method of claim 43, wherein a ratio of electrolytic zinc to particle-size-selected zinc in the mixture formed in the forming step is between about 1:9 and about 1:1.

45. The method of claim 43, wherein the electrolytic zinc and the particle-size-selected zinc, taken together, account for about 60% by weight of the mixture formed in the forming step.

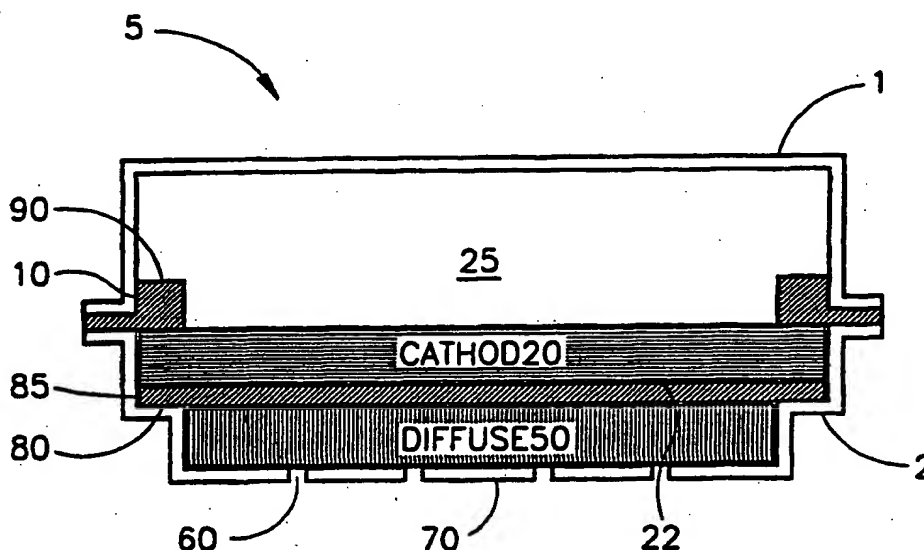
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(54) Title: CORROSION RESISTANT HIGH PERFORMANCE ELECTROCHEMICAL CELL



(57) Abstract

Particle-size-selected metal is mixed with an electrolyte and used as a combined anode/electrolyte in a metal-alkaline battery cell. The particles in the particle-size-selected metal are selected so that substantially all of the particles are larger than a predetermined size. The resulting battery cell exhibits improved corrosion and shock-resisting properties, as compared to when metal particles that have not been size-selected are used. In a preferred embodiment, zinc is used as the particle-size-selected metal to form a zinc-air battery.

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CORROSION RESISTANT HIGH PERFORMANCE ELECTROCHEMICAL CELL

CROSS REFERENCE TO RELATED APPLICATIONS

Priority is claimed to U.S. application No. U.S. application No. 60/112,292, filed on December 15, 1998; and U.S. application No. 60/129,401, filed on April 15, 1999, and each of these applications is incorporated herein by reference in its entirety.

BACKGROUND OF THE INVENTION

The present invention relates to zinc-based alloys and electrolyte additives providing resistance to corrosion and improved performance as an electrode in electrochemical cells.

The invention also relates to materials for housing electrochemical cells that ameliorate corrosion problems. The present invention is particularly applicable for zinc-based alloys for use in metal-air battery cells.

In conventional zinc-air batteries, the cathode reduces ambient oxygen, which means that the battery has only a single consumable electrode. The cathode of a metal-air battery typically has an active layer of activated carbon, a catalyst, and a binder, which forms a network and holds the carbon together. Embedded within the active layer is a metal current collector. A guard layer covers the surface of the active layer that faces the outside air, and an ionically conducting separator covers the surface that faces the anode. The guard layer keeps electrolyte from leaking out of the cell, and the separator separates the anode or an electrically conductive reaction product from the cathode active layer, thereby preventing an electrical short.

Polytetrafluoroethylene (PTFE) is an example of a suitable material for a binder, and manganese oxides and hydroxides are commonly used catalysts. A nickel screen is a commonly used current collector although an expanded metal sheet or an alternative conductive material can be used, instead. The guard layer can be made of a sheet of porous PTFE, and the separator can be made of a semipermeable membrane or a porous material.

Zinc-alkaline cells are known in the art as safe power sources having very high energy densities. One class of such cells - namely, zinc-air cells - can use ambient oxygen as one of their electrodes, which eliminates the need for such cells to house two consumable electrodes in the same casing. Along with the benefits of metal-alkaline cells comes the drawback of the anode's tendency to corrode, particularly in the presence of dissimilar metals and electrolytes. Also, metal-alkaline batteries suffer from relatively poor performance in low temperature environments.

One example of metal alkaline cells, namely zinc air cells, are capable of very high energy densities. The components of zinc-air cells are typically lightweight and inexpensive. Although zinc-air cells have high energy density, their power capacity is not extremely high and this is unfortunate since many electronic portable devices demand relatively large amounts of power from their power sources.

A known technique for enhancing power performance in metal-alkaline cells is to provide high reaction rates by subdividing the metal as finely as possible or using crystalline forms characterized by high surface to mass ratio. Electrolytic zinc derives its ability to increase its power through its very high surface area to mass ratio. Unfortunately, the higher surface area also contributes to increased corrosion rates. It is known to alloy metals such as zinc with metals that reduce the corrosion rate. However, electrolytic zinc cannot be alloyed easily because of the way it is formed.

Thermal zinc (powdered zinc formed by atomization) is susceptible to alloying. However, thermal zinc cannot, at present, approach electrolytic zinc's surface area to mass ratio.

Zinc-air battery cells typically have casings made, at least partly, of metal. The beneficial material properties of metal include its ability to serve the multiple purposes of housing the electrode(s), serving as electrical terminal(s) of the cell, and as providing a large surface area to act as a low resistance current collector. Its value as a housing material derives from its cost, manufacturability, strength, and other features. Cells can be made from two electrically insulated metal casing elements, which act as the opposing terminals of the cell, making the cell easy to electrically connect with an electronic device. Further, metal casings are inexpensive to manufacture, sometimes requiring only a simple stamping operation of a thin sheet of metal to form a relatively precisely shaped casing element.

Metal casings can exacerbate corrosion by forming a galvanic process with the zinc and the electrolyte. Corrosion wastes the cell's energy by consuming the zinc anode. Certain

agents have been found to reduce the corrosive effects. However, these corrosion-inhibiting agents create certain difficulties and tend to inhibit the power capacity of the cell.

The parasitic corrosion of zinc produces hydrogen gas. Hydrogen, if not permitted to escape from the casing of the cell, can cause the internal pressure of the cell to rise. An increase in the internal pressure of the cell can cause the cell to electrically short, swell, leak electrolyte, and potentially burst.

Zinc-air battery cells typically perform poorly in low temperature environments. As the temperature decreases, the viscosity of the electrolyte increases, which can lower the power capacity and overall energy capacity (given a minimum-voltage requirement for usability) of the cells.

Zinc-air battery cells are also susceptible to failure due to sudden shocks. Sudden shocks can significantly and temporarily reduce the discharge voltage of the cell. These shocks can cause the electronic device to temporarily lose power. In certain applications, a temporary loss of power can have significant adverse effects. For example, a transient loss of power in a cellular phone may result in disconnection.

SUMMARY OF THE INVENTION

It is a principal object of the invention to provide an electrochemical cell having zinc electrodes with improved corrosion resistance and higher performance, particularly at low temperatures. It is a further object of the invention to provide a metal casing that can eliminate or significantly inhibit the reactivity between a zinc-based anode and a metal casing.

Electrolytic zinc, with its high current generation potential, is mixed with thermal zinc, which can then be mixed with corrosion-inhibiting agents. In the alternative, the corrosion-inhibiting agents can also be alloyed with the thermal zinc, during its formation or otherwise, and then be combined with electrolytic zinc. In the formation of pure electrolytic zinc, the corrosion-inhibiting metals are less prone to alloy with the zinc anode. The addition of these agents significantly reduces the rate at which the zinc corrodes.

In certain mixtures of electrolytic/thermal zinc, the two types of zinc can be mixed together and pressed to form into a plaque. The formation of a plaque may eliminate the need to add a gelling agent. The result is a somewhat rigid structure that is capable of being placed in the cell instead of being extruded in the cell. The structure of the zinc significantly improves the manufacturability of the cell.

A typical tri-clad metal casing is made of layers of nickel, stainless steel, and copper, with the layer of copper on the inner surface of the casing element and the layer of nickel on the outer surface of the casing element. The combination provides strength via the stainless steel, better electrical connectivity through the addition of the nickel, and a reduction in the chemical reactivity between the layer of stainless steel and the zinc anode through the use of copper. A layer of tin on top of the layer of copper can further reduce the rate of corrosive activity by separating the zinc/electrolyte mixture from the metal casing. This layer can be added by soldering, electrolytic plating, or by an electroless process.

The performance of the zinc anode, especially in low temperature environments, can improve through the addition of low viscosity diluents and/or alumina. The addition of diluents such as isopropanol have been found to increase the discharge voltage of the cell with a minor decrease in energy capacity. The addition of alumina increases the energy capacity of the cell by up to 20%. The combination provides both benefits.

The invention will be described in connection with certain preferred embodiments, with reference to the following illustrative figures so that it may be more fully understood.

With reference to the figures, it is stressed that the particulars shown are by way of example and for purposes of illustrative discussion of the preferred embodiments of the present invention only, and are presented in the cause of providing what is believed to be the most useful and readily understood description of the principles and conceptual aspects of the invention. In this regard, no attempt is made to show structural details of the invention in more detail than is necessary for a fundamental understanding of the invention, the description taken with the drawings making apparent to those skilled in the art how the several forms of the invention may be embodied in practice.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is graphical representation of discharge voltages of two similarly sized battery cells with zinc anodes having a different porosity.

Fig. 2 is graphical representation of the discharge voltages of five similarly sized battery cells with zinc anodes having different porosity and polyethylene glycol (PEG) content. The representation shows the effect that a sudden jolt has on differently configured battery cells.

Figs. 3 and 4 show the effect that the additions of a diluent and alumina to a metal

anode have on the performance of a battery cell exposed to a low temperature environment.

Fig. 5 shows a cross-sectional representation of a tri-clad metal anode casing element of successive layers of nickel, stainless steel, and copper.

Fig. 6 shows an alternative cross-sectional representation of a tri-clad metal anode casing element with a layer of copper on both sides of a layer of stainless steel.

Fig. 7 is a schematic section view of a typical zinc-air battery cell that can make use of the air cathode of the present invention. The schematic is intended only to illustrate relationships between various components.

Fig. 8 is schematic section, partial perspective, view of an air cathode illustrating some of the embodiments of the invention.

DESCRIPTION OF THE INVENTION

The cathode described herein is intended for use in electrochemical cells or fuel cells. It is especially intended for use in primary metal-air battery cells, and especially zinc-air cells. The cells may be any suitable shape and be arranged in a housing that is liberally supplied with openings to allow air gases to be exchanged between the ambient air and the enclosed cells. The cells can have a housing of metal, plastic, or any other suitable material. Each cell may have an array of air holes, such as used in zinc-air button cells, in such number and size as to allow oxygen to be supplied to a cathode inside the cell. The air holes of each cell may face either a plenum or the casing wall. The air holes are uniformly distributed, sized, and present in such number so as to insure that the cathode is not starved for oxygen, which could cause a drop in voltage. As an alternative to holes, the cell may use a semipermeable membrane or structure that permits the diffusion of gases through the membrane or structure.

Referring to Fig. 7, each of the cells 5 contains at least one air cathode 20 and at least one zinc anode 25 with aqueous alkaline electrolyte (e.g., KOH). The cathode 20 lies adjacent a cathode side of the cell casing 2 and may be separated from that side by a diffuser 50. The diffuser 50 distributes oxygen from holes 60 in the cathode side of the cell 2 across the surface of the cathode 20 and keeps the cathode 20 at a fixed distance, equal to the diffuser's 50 thickness, from the cathode side 2 of the cell 5. The diffuser 50 may be a porous material such as woven, knitted, or non-woven cloth or extended plastic mesh material. It may act as a standoff to prevent the air-side surface 22 of the cathode 20 from smothering any of the holes 60 when an expansion of the zinc anode 25 causes the surface to press against the

inside wall of the cathode side of the cell 2. The holes 60 in the cathode side of the cell 2 are uniformly distributed across the primary plane 70 of the cathode side of the cell.

The casing 1 / 2 of the cell may be formed in two halves, an anode side 1 and a cathode side 2 as in Fig. 7. The cell casing 1 / 2, may be formed of any suitable material. If the casing 1 / 2 is made of metal or any other conductive material, the two halves 1 and 2 should be insulated from one another. In either case, to form a primary seal 80, the cathode 20 may be attached to, or sealed against, the cathode side 2 of the cell casing 1 / 2. The primary seal 80 may be effected by pressure, adhesive, or any other suitable means to prevent liquid electrolyte from leaking into the space occupied by the diffuser 50. That is, the primary seal 80 prevents liquid electrolyte from seeping around the cathode 20 into the area exposed to the outside air. A secondary seal 10 between the anode side of the cell 1 and the cathode side 2 prevents aqueous electrolyte from seeping around to the edge of the cathode 20 or leaking out of the cell 5. In the embodiment of Fig. 7, the secondary seal 10 is formed by a grommet 90, which also serves to insulate the anode side 1 and cathode side 2 of the cell casing 1 / 2 from each other. Pressure, an adhesive, or flowing sealant, or other suitable means may be used to effect the secondary seal 10.

Referring to Fig. 8, in an embodiment, the cathode consists of multiple layers with the middle layer being an active layer 120 composed primarily of carbon, PTFE, and a catalyst for reducing oxygen. Note that Fig. 8 is not to scale. The active layer 120 is the location where the oxygen reduction reaction takes place in the presence of the catalyst. A separator layer 100 which may be prelaminated to the active layer 120 can be made from microporous hydrophilic polypropylene (PP), polyethylene, PVC, cellophane, nylon, Celgard®, or other materials exhibiting similar properties. In some applications, the pore size of the separator 100 is in the range of about 0.25 micron to 2 microns instead of the more typical average pore size of less than 0.25 micron used in other battery applications. The larger pore size is sufficient to limit electrical shorts from crystallization of zinc oxide in the separator layer 100, and still permit enhanced wetting of the cathode active layer 120 with KOH solution. Other types of separator materials that may provide better cathode performance include microporous polyethylene or polypropylene whose hydrophilicities are enhanced by radiation grafting. Another class of suitable separator materials is semipermeable membranes based on cellophane, polyethylene, PVC, nylon, and polypropylene, for example, ZAMM-0 supplied by Pall RAI Corp. An additional non-woven, absorbent material can be added between the air

electrode and the microporous separator or between the microporous separator and the zinc. The purpose of this is to provide an electrolyte reservoir.

The following processes may provide the preferred composition of the electrode active layer 120. The quantities are representative only and the quantities and proportions may be varied.

1. 240 g MnO_2 powder (Aldrich Chemical Company, Milwaukee, WI) is milled for 24 hours.
2. Add 2000 cc deionized water and heat to 85°C while stirring.
3. Slowly add 800 g activated carbon (Darco G-60 from American Norit, Atlanta GA).
4. Slowly add 288 cc PTFE suspension (grade 30-N from DuPont).
5. Continue stirring for an hour.
6. Filter and then dry at 120°C for about 5 hours.

An alternative process for making an active layer that starts with KMnO_4 instead of MnO_2 is described in US Patent 3,948,684, the entirety of which is incorporated herein by reference.

Embedded within the active layer 120 is a current collector 140 commonly formed of a metal, for example, a nickel, screen. Nickel-plated or nickel-clad steel, gold-plated metal, or other materials could also be used. A plastic element coated or clad with a conductor could even be used. It is preferred that the current collector 140 of the cathode be treated or constructed in such a way as to provide high surface area and low electrical resistance. The formation of oxide on the surface of a metal mesh current collector or a thin film of electrolyte on the hydrophilic surface of the current collector may limit the power capacity of the battery cell. One way to deal with this is to coat the current collector with a coating of a non-corroding metal finish. However, merely coating the current collector will not eliminate the disadvantages of remaining hydrophilic. Another option is to paint the electrode with a hydrophobic conductive paint. Hydrophobic conductive paints have other advantages over metal finishes. Gold and silver are the only metals that can be coated on a cathode mesh and still provide reasonable conductivity. Both are very expensive. Moreover, a silver coating is slightly soluble in alkaline electrolytes, which may lead to an increased corrosion of the zinc anode.

This paint may be applied before the cathode active layer is combined with the current collector. A preferred paint is a mixture of the following:

1. Fluorinated ethylene propylene copolymer (FEP) (Dupont 120-N or 121A) or some other thermoplastic, (e.g. polyolefin) preferably a fluoropolymer.
2. Isopropyl alcohol or some other suitable solvent (other alcohols, ketones, chlorinated hydrocarbons, etc.)
3. Acetylene carbon (Shawinigan carbon black made by Chevron) or some other suitable form of carbon, preferably hydrophobic, such as graphite.

A representative batch of paint may be formed of 1400 cc isopropyl alcohol, 108 cc FEP and 20 g acetylene black. The paint may be sprayed, or applied by any alternative suitable means, onto a mesh at a loading of 0.72 mg/cm^2 . This loading is only an example, and higher or lower loading values may also be used. The coated mesh is then baked in an oven at $290\text{--}330^\circ\text{C}$ to sinter the FEP and bond it to the metal current collector, e.g., woven nickel mesh. The actual sintering temperature, in applications of the present invention, may depend upon the particular thermoplastic used. Note that, in addition to sintering a sinterable material such as FEP, materials that can be melted to form a coherent mass could also be used in replacement of the sinterable material to bond the coating in place. The painted current collector may be heated by microwave, infrared, RF, or ultrasonic means instead of heating the coated mesh in an oven. The sintered coating forms a continuous hydrophobic conducting coating that protects against the corrosion or the oxidation of the metal mesh material. The sintering step also removes the surfactant in the FEP emulsion. It has been found that an air electrode with this coating laminated to a suitable separator and then incorporated into a zinc-air cell of area 10 cm^2 (2.5 cm. by 4 cm.) gave a steady state voltage 250 mV higher than an air electrode without this coating when discharged at a constant 0.47A.

To provide for high current capability in zinc-air batteries, the cathode should be fully saturated with electrolyte. The cathode tends to dry out as a result of water evaporating from the cell and as a result of waters of hydration being drawn away from the cathode when zinc oxide forms during discharge of the cell. The addition of hydrophilic agents to the cathode ameliorates this dryout effect. For example, cellulosic materials such as Natrosol® 250 MBR hydroxyethylcellulose (HEC) may be added to the cathode material (finely divided and added to the active layer mixture). As moisture leaves the cathode during discharge, the HEC holds onto this moisture and makes it available in the cathode despite the progressive drying of the cathode. A similar material has been used as a monolithic layer, but the incorporation

of the material in its finely divided form inside the cathode active layer helps to insure that moisture is held where it is needed. The following is an example construction of a cathode material using Natrosol.

5 240 g. of MnO_2 powder (Aldrich Chemical Company, Milwaukee, WI) is ground finely in a mill for 24 hours. The MnO_2 is then poured into 2 liters of deionized (DI) water and heated to 85°C . Add 800 g. of Darco G-60 carbon (American Norit, Atlanta GA) while stirring. Then add 288cc of Dupont 30-N PTFE suspension. Continue stirring for one hour, and then filter and dry at 120°C for 5
10 hours.

 Slowly add 200g of the active mass made above to 5 liters of DI water stirred at 85°C . After all the carbon is in suspension, add 2 grams of Natrosol (grade 250MBR from Hercules). Continue stirring under heat until dry.

 The active mass treated with the Natrosol® is spread evenly over a
15 nickel mesh (40x40 mesh 0.005 mm dia. nickel from National Standard) and pressed to make an active layer of an air electrode. A porous PTFE sheet is then pressed on one side of the active layer.

 The air electrode from above is then laminated with a microporous polypropylene film (grade 3501 from Celgard®) separator. The air electrode and separator laminate is then assembled into a zinc-air cell of area 10cm^2 containing 3.1g
20 zinc and 2.4g 8M KOH solution, and the complete cell closed by crimping.

 Testing Technique – The test cell and a control cell that does not contain the Natrosol® are exposed to a 25-30% relative humidity (RH) environment for a period of 7 days. After 7 days the cells are discharged under a load following a
25 GSM profile, which is one of the standard profiles used by mobile communication devices for communicating with ground stations. GSM is a galvanostatic square wave profile consisting of 1.3A for 0.6 msec and 0.08A for 4.0 msec. The discharge cycle spans one hour (0.2Ah). The cells are then returned to the low humidity environment. This discharge cycle is repeated every 3-4 days until the cells fail. Failure is defined
30 as the high current voltage falling below 0.9V.

 Results - On the initial test after 7 days, both types of cells had a voltage above 0.9V. But when tested after a total of 11 days exposure to 25%RH, the

cell without Natrosol® failed. The cell with Natrosol® continued to work in similar tests over a period totaling 25 days in a 25%RH environment.

In Fig. 8, which shows a cross-section of the cathode, there is a guard layer 160, preferably formed of a PTFE film, laminated to the side of the active layer facing the air holes. The guard layer 160 allows oxygen to enter the cathode while preventing liquid electrolyte from leaking out. This layer 160 is preferably unsintered and highly porous to gases. The preferred porosity is at least 30%, but it is desirable to provide a guard layer that is even more porous. Porosity of 50% or more are even more preferable. The preferred thickness of the guard layer is no more than 100 microns.

As visible in Fig. 7, an uncompressed PTFE film 85, which is separate from the laminated structure of the cathode 20, is uncompressed by any laminating process used to form the cathode structure shown in Fig. 8. During the manufacture of the cell, the grommet 90 forces the cathode 20 against the cathode side of the cell 2, thereby compressing the previously uncompressed PTFE film 85. This helps to form the primary seal 80, which isolates the volume of the cell that is in communication with the outside air from the electrolyte as described above. Since the film 85 is initially uncompressed, it can act as a gasket to create or augment the secondary seal. Also, as discussed above, other means may be used to effect the seal 80 and the uncompressed PTFE layer 85 is not essential for this purpose. The PTFE layers – the guard layer laminated to the cathode and the uncompressed layer – allow air to diffuse into the cathode while preventing liquid from leaking out.

In production, the active layer 120, the separator sheet 100, and the guard layer 160 may be laminated together to form a single structure. Representatively, the dimensions of the active layer and the separator layers are 0.20-0.50 mm and 0.025-0.25 mm, respectively. The actual dimensions depend on the application and can be any suitable thickness. It is preferable that the final pressure used to laminate all the layers together not be too high.

It has been found that an active layer density of less than 1 g/cc is a suitable for attaining high current densities. It has been found that an active layer density of 0.8 g/cc is achievable and provides even greater current density potential. It was found that a PTFE layer with a porosity greater than 50% and a thickness less than 100 microns and an active layer with a density less than 1 g/cc, and preferably less than 0.8 g/cc, exhibits a substantially higher limiting current than prior art cathodes. Together, these improvements produce an air electrode with a limiting current greater than 400mA/cm² with a voltage greater than -300mV as compared to a Hg/HgO reference electrode at room temperature.

Still another feature that has been found to result in higher performance is a roughened surface on the cathode active layer facing the separator. Such a surface can be obtained by pressing the surface with an irregularly surfaced mold to form an imprint. Alternatively, various abrasion techniques, such as brushing, air blasting, or sandblasting; or various heat treatments, such as partial oxidation, can be used. The average roughness (R_a) of the surface, as measured by ANSI B46.1-1978, should be on the order of 10-100 microns instead of the usual 0.1-1 microns.

The combining of thermal zinc and electrolytic zinc to form a zinc mixture results in a zinc anode that is capable of generating relatively high current and combining with many performance increasing additives, such as corrosion inhibiting agents. Electrolytic zinc is formed by subjecting zinc to an electrolytic process, which results in a form of zinc that is porous and that has a high surface to mass ratio. The process includes directly electroplating metallic zinc onto a current collector from a solution of zinc ions. The porous zinc that results from the process exhibits superior electrical conductivity and is capable of generating more power than a less porous zinc. Referring to Fig. 1, the graph plots the voltage output over time of two battery cells subjected to the same load. Line A represents the voltage output of a battery cell containing electrolytic zinc, and line B represents a battery cell containing thermal zinc. Fig. 1 clearly shows that electrolytic zinc (Line A) provides an increase of approximately 0.2 volts or approximately 20% to the voltage output of the battery cell.

Although the electrolytic process is beneficial in that it results in a zinc capable of generating high current, the electrolytic process is not suitable for forming particles containing corrosion inhibiting metals alloyed to the zinc. Thermal zinc, on the other hand, is capable of combining with corrosion inhibiting agents and is formed by atomizing molten zinc to form a zinc powder having a particle size distribution of between 0.0075 to 0.8 mm and a surface area of between 0.2 – 0.4 m²/g. Thermal zinc can then be combined with corrosion inhibitors, a gelling agent and a KOH solution to form a gelled mass capable of being extruded to form a zinc anode.

A mixture of thermal zinc with electrolytic zinc results in a combination exhibiting beneficial qualities of both thermal and electrolytic zinc. A gelling agent may be added to the mixture to form a zinc slurry. A mixture containing 10% to 50% electrolytic zinc is preferable.

At the higher end of the spectrum (50% electrolytic zinc), a gelling agent may not be necessary. The mixture can be combined and pressed together to form a porous, rigid, plaque.

The plaque maintains its shape due to the dendritic structure of electrolytic zinc tangling with the structure of the thermal zinc. The dendritic branches of electrolytic zinc tangle with each other and also with the thermal zinc to hold the powder-like thermal zinc. One advantage of forming a plaque structure is that the plaque can be placed in the casing. Normally, a gel-like, zinc bolus is dispensed in the casing and the manufacturer must provide time in the assembly process for the zinc to settle and spread out to fill the casing.

The addition of polyethylene glycol (PEG) to the zinc electrolyte mixture can reduce the rate by which the zinc corrodes. The effect of PEG on zinc corrosion was evaluated using PEGs with differing molecular weights. Referring to Table 1 below, PEG-600 and PEG-1500 were found to be most effective in this demonstration, with higher concentrations resulting in better corrosion resistance.

TABLE 1

Concentration, ppm	Corrosion rate (%/week)		
	PEG-600	PEG-1500	PEG-10,000
500	0.009	0.007	0.017
1000	0.008		0.018
1500	0.006	0.006	0.017
2500	0.005	0.006	0.018
3000	0.006	0.006	0.018
4000	0.004	0.004	0.017
5000	0.002	0.004	0.016

The addition of PEG to the zinc anode also increases the cell's resistance to sudden shocks. Sudden mechanical shocks to the cell can cause the discharge voltage to significantly and temporarily drop. This voltage drop can significantly and adversely affect the operation of the device powered by the cell. The effect is more pronounced in zinc-air cells with zinc anodes made of electrolytic zinc.

A large minimum particle size can contribute substantially to a low corrosion rate. A particular zinc anode material was obtained by removing the smallest fraction of particles, those below 100 microns, from a batch of zinc particles. In test samples, the starting material

was Mitsui thermal zinc, 50 to 500 microns. The smallest fraction, below 75 microns, was removed by sieving. The results of tests of samples of the big zinc particles shows a very low corrosion rate. The following are results of corrosion tests on various batches of zinc material, some in combination with PEG or PbO.

5

Table 2

No	Type	IR	Rp	V _{plat}	Cap [Ah]	Corrosion rate (%/wk)		
						0%	20%	50%
1	Small particles- 38-75 μ	.055	30	1.1	2.3	0.23	0.34	0.9
2	Big particles- 250-500 μ	0.08	150	1.13	2.7	0.04	0.2	0.35
3	100 ppm PEG	0.07	880	1.01	2.6	0.05	.021	0.28
4	200 ppm PEG	0.1	1150	1.055	2.35	0.05	.011	0.2
5	In coating	0.1	80	1.11	2.55	0.15	.02	0.5
6	500 ppm PbO	0.1	70	1.04	2.6	0.25	.04	-

Six samples were tested. The first sample consisted of small particles of zinc in the range of 38-75 microns. The rest of the samples contained large particles of zinc in the range of 250-500 microns. The second sample had no additives. The third and fourth contained 100 and 200 ppm PEG-600 in the electrolyte. The fifth sample had an indium-coated lining adjacent the zinc. The sixth sample contained 500 ppm PbO. Table 1 shows the results corrosion tests in which the cells were discharged at 0.47 A. The table headings are defined as follows: IR is the resistance of the test cell. Rp is the passivation resistance. V_{plat} is the plateau exhibited by the voltage vs. time discharge curve. Cap. is the total energy delivered before the voltage dropped below 0.9 volts. Corrosion rates were measured at various points through the discharge history of the test cells, namely, at 0% discharge, 20% discharge, and 50% discharge.

From Table 2 it can be seen that the corrosion rate of small particles is much greater than that of the larger particles. Addition of PEG reduced corrosion but reduced the plateau voltage and increased the passivation resistance. From these data, it is concluded that removing the smaller fraction of zinc from a batch of zinc particles reduces the corrosion rate. It has been found by further experiments that if the particles below 75 microns are removed

from a zinc batch, the corrosion rate is lowered to the point comparable to the above large particle samples. Preferably, the particles below 100 microns in size are removed.

Fig. 2 shows the effects of mechanical shocks on the discharge voltage of five (5) zinc-air battery cells, A, B, C, D, and E, having different proportions of PEG and having different porosities (the greater the concentration of PEG corresponds to lesser porosity). At times I, II, and III, the battery cells were dropped onto a rigid surface at increasing heights. As shown in the chart, PEG affects the cell's reaction to shock. At concentrations of 10 ppm, the battery cell experienced a drop of .135 volts or approximately 10% when dropped from a height of 10 cm. This drop was less than .02 volts, or 2%, when the PEG concentration was increased to 50 ppm. Increasing the concentration further results in a minor improvement in shock resistance with a significant drop in discharge voltage. Although the discharge voltage of the 10 ppm. cell benefited from the lower concentration levels, this benefit was more than offset by the shock effects when dropped more than 10 cm.

To increase the performance of the cell, especially when exposed to low temperatures, a low viscosity diluent can be added to the zinc electrolyte mixture. Examples of suitable diluents are isopropanol, isobutanol, and secbutanol, and long chain and branched alcohols. Concentrations of 5% by weight of a low viscosity diluent have been found to increase the discharge voltage by 60mV.

To increase the energy capacity of the cell, alumina (Al_2O_3) can be added to the zinc mixture. Concentrations of alumina of 1% by weight have been found to increase capacity by about 10%. However, the addition of alumina tends to decrease the discharge voltage of the cell. This voltage decrease can be offset through the addition of a diluent, as described above.

Referring to Figs. 3 and 4, the two graphs show the effects that alumina and isopropanol have on a battery cell when the battery cell is exposed to low temperature environments.

Figure 3 shows the discharge voltage of a battery cell with the additives at 25°C, and Figure 4 shows an identically-configured cell at 0°C. In the lower temperature environment (Fig. 4), both the discharge voltage and the energy capacity of a cell with the additives exceeded those of the cell without the additives. In the higher temperature environment (Fig. 3) the additives neither helped nor hurt the performance of the battery cell.

Corrosion resistance of the zinc anode is also accomplished through a coating on the metal casing. The zinc anode can react galvanically with the metal of the casing, resulting in corrosion and the generation of hydrogen (gassing). Gassing increases the internal pressure of the battery cell, which also increases the likelihood that the battery cell will leak. The

generation of hydrogen can cause a cell to fail within hours of assembly.

The following zinc/electrolyte/corrosion-inhibitor combination was formed as an example that displays the above properties.

1. 560 grams of zinc powder (thermal zinc) from Mitsui Mining & Smelting Co. Ltd., ABI grade is mixed with 5 grams of Carbopol 941, a gelling agent, to form a uniform zinc/gelling agent mixture.

2. 27.4 grams of ZnO from Durham, Electrolux grade, is mixed with a liter of deionized water, 8.5 M in KOH, to form zincate solution. Electrolytic zinc is formed by electroplating the zinc from the zincate solution onto a metal sheet. The electrolytic zinc is added to 435 grams of a deionized water solution of 8.5 M KOH from Oxychem Co. at a proportion of 22 grams of electrolytic zinc for every liter of deionized water to form a zinc/water solution.

3. The zinc water solution is mixed with the zinc/gelling agent mixture to form a blend containing 56.0:0.5:43.5 by weight of zinc powder:Carbopol:KOH. The blend is stored for 24 hours and separated into the desired dosage.

To limit gassing and corrosion, a layer of tin is coated onto the interior side of the casing, thereby separating the zinc anode from the metal casing. A complete electrical separation is not preferred since, in most zinc-air cells, the casing acts as an current collector of the cell, and the anode is electrically connected to this current collector through its contact with the casing.

The thickness and the manner of application play major roles in the effectiveness of the coating. Tests conducted on cells with a coating of indium of 11 microns and 33 microns revealed that the corrosion rate improved 320% - 900% from the thinner to the thicker coating. The average corrosion rate of a cell with a 11 microns thick coating of indium was 0.32% to 0.36% per week. This average decreased to 0.04% to 0.1% for a 33 microns thick coating.

Forming a uniform and complete coating of tin can be accomplished by soldering, electrolytic plating, and electroless plating. Tin can be soldered onto the surface of the casing by melting the tin and spreading it over one or both surfaces. Tin can also be added by an electrolytic process on either or both sides of the casing element. An electroless process can also be used. Applying tin through a well-known electroless process requires the presence of a copper support layer.

Referring now to Fig. 5 showing an anode casing element 100 formed of three layers of different materials, a layer of copper 105 forms the inner surface of the casing element 100, and a layer of nickel 110 forms the outer surface of the casing element 100. Between the two layers 105, 110 is a layer of stainless steel 115. The combination of the three layers 105, 110, and 115 provides the casing element 100 with material properties that are not found in a single material. The layer of nickel 110 provides the casing element 100 with improved electrical connectivity properties with the electronic device. The layer of nickel 110 also protects the layer of stainless steel 115 from the atmospheric conditions, which can cause the layer 115 to oxidize and corrode. The layer of stainless steel 115 provides strength to the structure of the casing element 100. The layer of copper 105 protects the layer of stainless steel 115 and the metal anode from reacting with each other and also provides a surface for the electroless plating of the protective layer of tin.

Copper is required for the electroless plating of tin. SnO or SnCl_2 reacts with the copper layer 105 in a bath containing thiourea. The layer of tin (not shown) formed on the copper layer 105 has been found to inhibit the corrosion of the metal anode.

The casing element 100 may also be formed of two layers instead of three, with the layer of nickel 110 eliminated. The nickel layer 110 does not assist with the inhibition of the reactivity between the zinc anode and the casing element 110, and is therefore, not absolutely essential to the benefit exhibited.

Further, a casing element may also have two layers of copper and one layer of stainless steel. For example, referring to Fig. 6 showing such an arrangement in an alternative casing element 120, a layer of copper 125 forms the inner surface of the casing element 120 and a layer of copper 125 also forms the outer surface of the casing element 120, with the copper layers 125 sandwiching a layer of stainless steel 130.

When this casing element 120 is immersed in a bath containing thiourea and SnO or SnCl_2 , layers of tin (not shown) are formed on both sides of the casing element 120. The layer of tin on the outer surface of the casing element 120 protects the casing element from corrosion in ambient air.

Another solution to the corrosion problem is to coat a substantial portion of the inner surface of the casing element with an insulator, such as an epoxy. Since the chemical reaction rate between the zinc anode and the casing element is directly related to the area of the exposed surface of the casing element to the zinc anode, a reduction of this exposed surface area reduces the rate of corrosion. However, some exposure should remain since the casing

element acts as a current collector of the cell, and electrical connectivity between the zinc anode and casing element should remain for the casing element to perform this function. Examples of suitable insulting materials include tar and epoxy.

To further improve the performance the efficiency of the battery cell, a zinc/electrolyte mixture should contain a lesser concentration of zinc than the mixture employed in the prior art. Concentrations of 60% zinc by weight, instead of 70-80% zinc as used in the prior art, ensures that a greater portion of the zinc is utilized. Larger concentrations of zinc results in a drier mixture that is more susceptible to desiccation and the attendant decreased energy capacity. Metal-air battery cells are particularly susceptible to dry-out.

It will be evident to those skilled in the art that the invention is not limited to the details of the foregoing illustrative embodiments, and that the present invention may be embodied in other specific forms without departing from the spirit or essential attributes thereof. The present embodiments are therefore to be considered in all respects as illustrative and not restrictive, the scope of the invention being indicated by the appended claims rather than by the foregoing description, and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced therein.

What is claimed is:

1. A metal-alkaline battery cell comprising:
a cathode including a catalyst and a conductive material;
5 a first terminal electrically connected to the cathode;
a mixture including an electrolyte and particle-size-selected metal;
a second terminal electrically connected to the mixture; and
a separator located between the cathode and the mixture, in physical contact with the
cathode and with the mixture, said separator being of such material as to permit ions to travel
10 between the cathode and the mixture and to block metal particles from contacting the cathode,
wherein substantially all particles contained in the particle-size-selected metal are
larger than a predetermined size.
2. The battery cell of claim 1, wherein the wherein the particle-size-selected metal
15 includes particle-size-selected zinc.
3. The battery cell of claim 2, wherein the particle-size-selected zinc accounts for about
60% of the mixture by weight.
- 20 4. The battery cell of claim 2, wherein the mixture includes electrolytic zinc.
5. The battery cell of claim 4, wherein a ratio of electrolytic zinc to particle-size-selected
zinc in the mixture is between about 1:9 and about 1:1.
- 25 6. The battery cell of claim 4, wherein the electrolytic zinc and the particle-size-selected
zinc, taken together, account for about 60% of the mixture by weight.
7. The battery cell of claim 1, wherein the conductive material includes carbon.
- 30 8. The battery cell of claim 1, wherein the wherein the separator includes Teflon.
9. The battery cell of claim 1, wherein the mixture includes a gelling agent.

10. The battery cell of claim 1, wherein the particle-size-selected metal contains a substantial amount of particles with sizes that are close to the predetermined size.

11. The battery cell of claim 10, wherein the predetermined size is about 75 microns.

12. The battery cell of claim 11, wherein substantially all particles contained in the particle-size-selected metal are smaller than about 500 microns.

13. The battery cell of claim 10, wherein the predetermined size is about 100 microns.

14. The battery cell of claim 13, wherein substantially all particles contained in the particle-size-selected metal are smaller than about 500 microns.

15. The battery cell of claim 1, wherein a corrosion-inhibiting agent is alloyed in the particle-size-selected metal.

16. A metal-air battery cell comprising:

an air electrode;

a first terminal electrically connected to the air electrode;

a mixture including an electrolyte and particle-size-selected metal;

a second terminal electrically connected to the mixture; and

a separator located between the air electrode and the mixture, in physical contact with the air electrode and with the mixture, said separator being of such material as to permit ions to travel between the air electrode and the mixture and to block metal particles from contacting the air electrode,

wherein substantially all particles contained in the particle-size-selected metal are larger than a predetermined size.

17. The battery cell of claim 16, wherein the separator includes Teflon.

18. The battery cell of claim 16, wherein the particle-size-selected metal includes particle-size-selected zinc.

19. The battery cell of claim 18, wherein the particle-size-selected zinc contains a substantial amount of particles with sizes that are close to the predetermined size.

20. The battery cell of claim 19, wherein the predetermined size is about 75 microns.

21. The battery cell of claim 20, wherein substantially all particles contained in the particle-size-selected zinc are smaller than about 500 microns.

22. The battery cell of claim 19, wherein the predetermined size is about 100 microns.

23. The battery cell of claim 22, wherein substantially all particles contained in the particle-size-selected zinc are smaller than about 500 microns.

24. The battery cell of claim 19, wherein the mixture includes a gelling agent.

25. The battery cell of claim 19, wherein a corrosion-inhibiting agent is alloyed in the particle-size-selected zinc.

26. The battery cell of claim 19, wherein the particle-size-selected zinc accounts for about 60% of the mixture by weight.

27. The battery cell of claim 19, wherein the mixture includes electrolytic zinc.

28. The battery cell of claim 27, wherein a ratio of electrolytic zinc to particle-size-selected zinc in the mixture is between about 1:9 and about 1:1.

29. The battery cell of claim 27, wherein the electrolytic zinc and the particle-size-selected zinc, taken together, account for about 60% of the mixture by weight.

30. A method of forming a corrosion resistant metal-air battery cell comprising the steps of:

forming a mixture by mixing ingredients including an electrolyte and particle-size-selected metal;

electrically connecting a first terminal to the mixture obtained in the forming step;
obtaining an air electrode with a second terminal connected thereto; and
positioning a separator between the air electrode and the mixture, in physical contact
with the air electrode and with the mixture, wherein the separator permits ions to travel
5 between the air electrode and the mixture and blocks metal particles from contacting the air
electrode,

wherein substantially all particles contained in the particle-size-selected zinc are larger
than a predetermined size.

10 31. The method of claim 30, wherein the particle-size-selected metal contains a substantial
amount of particles with sizes that are close to the predetermined size.

32. The method of claim 31, wherein the predetermined size is about 75 microns.

15 33. The method of claim 32, wherein the particle-size-selected metal includes particle-
size-selected zinc.

34. The method of claim 32, wherein substantially all particles contained in the particle-
size-selected metal are smaller than about 500 microns.

20

35. The method of claim 31, wherein the predetermined size is about 100 microns.

36. The method of claim 35, wherein the particle-size-selected metal includes particle-
size-selected zinc.

25

37. The method of claim 35, wherein substantially all particles contained in the particle-
size-selected metal are smaller than about 500 microns.

38. The method of claim 31, wherein the particle-size-selected metal is obtained by
30 removing substantially all metal particles that are smaller than the predetermined size from a
batch of metal particles.

39. The method of claim 38, wherein a sieve is used to remove substantially all of the

metal particles that are smaller than the predetermined size.

40. The method of claim 31, wherein the mixture formed in the forming step includes a gelling agent.

5

41. The method of claim 31, wherein a corrosion-inhibiting agent is alloyed in the particle-size-selected metal.

42. The method of claim 31, wherein the particle-size-selected metal includes particle-size-selected zinc, and the particle-size-selected zinc accounts for about 60% by weight of the mixture formed in the forming step.

10

43. The method of claim 31, wherein the particle-size-selected metal includes particle-size-selected zinc, and the mixture formed in the forming step includes electrolytic zinc.

15

44. The method of claim 43, wherein a ratio of electrolytic zinc to particle-size-selected zinc in the mixture formed in the forming step is between about 1:9 and about 1:1.

45. The method of claim 43, wherein the electrolytic zinc and the particle-size-selected zinc, taken together, account for about 60% by weight of the mixture formed in the forming step.

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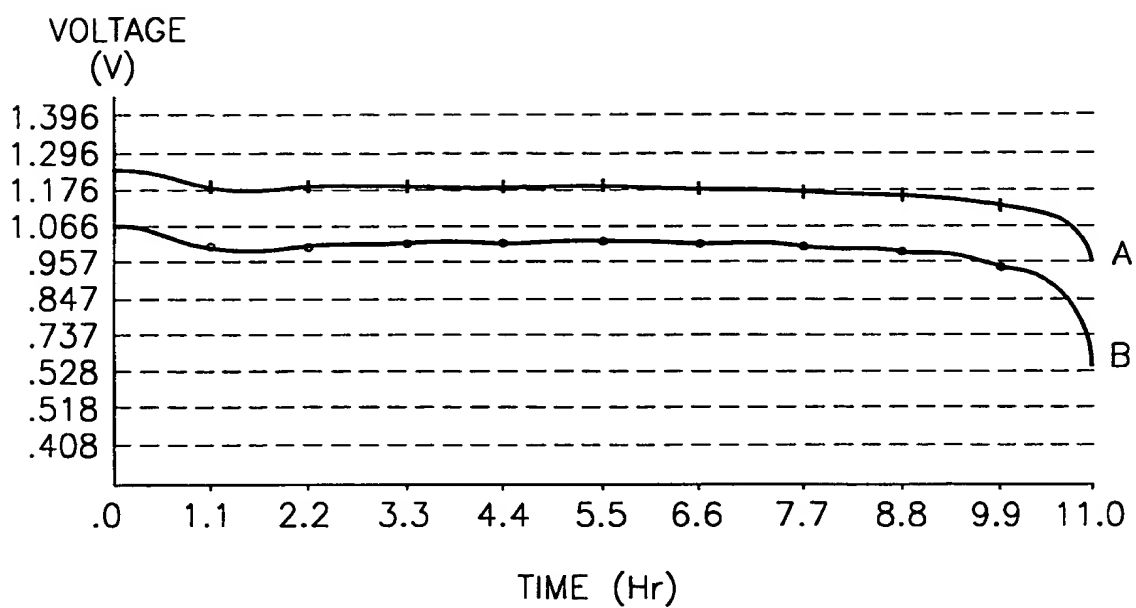


FIG.1

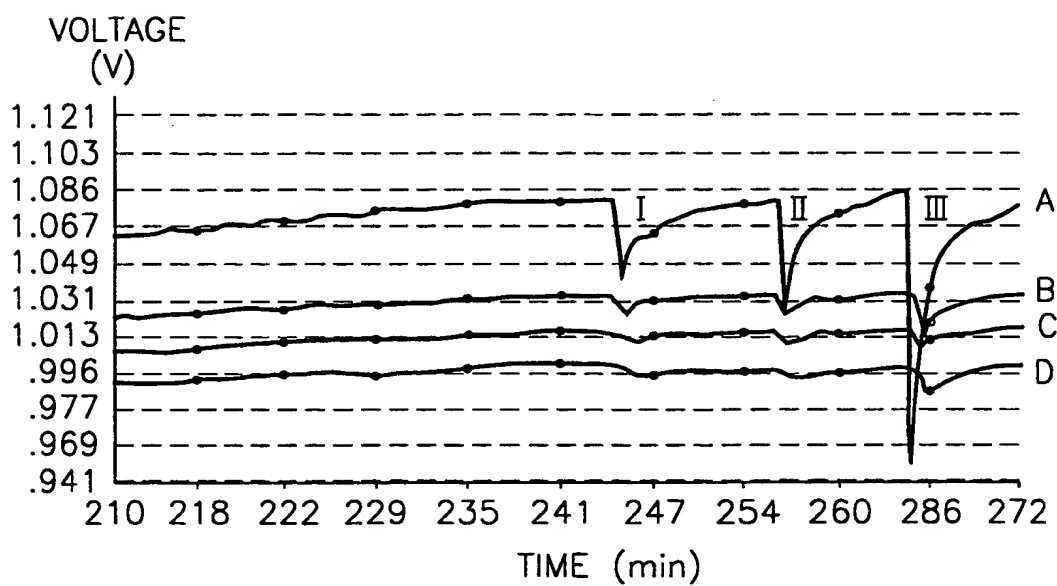


FIG.2

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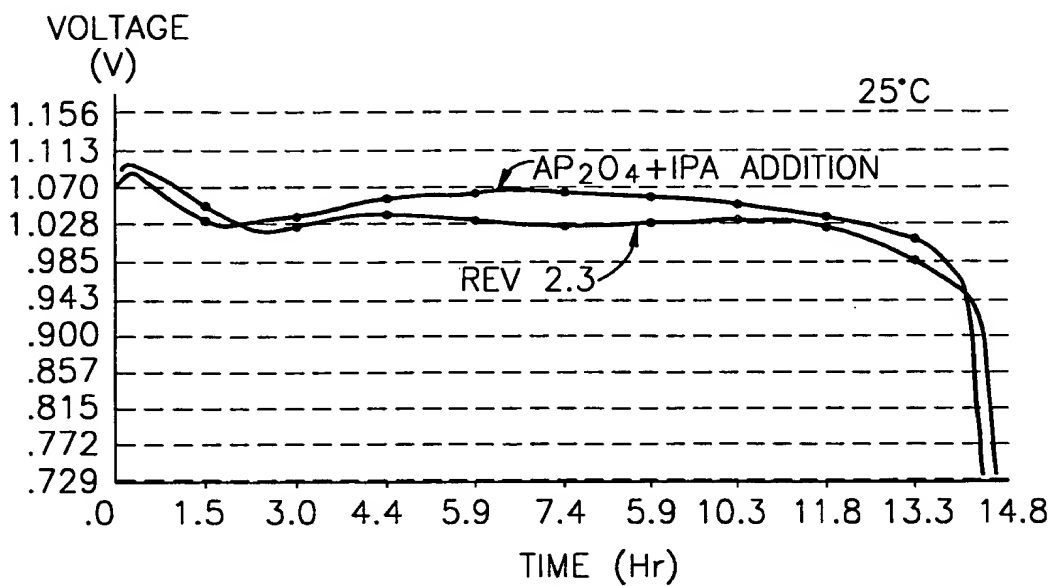


FIG. 3

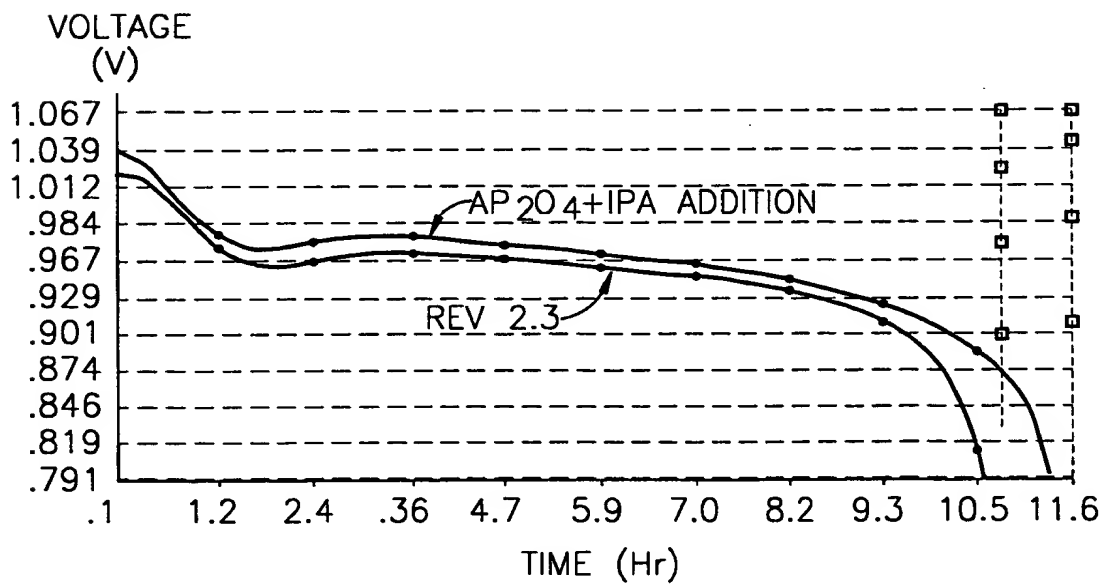


FIG. 4

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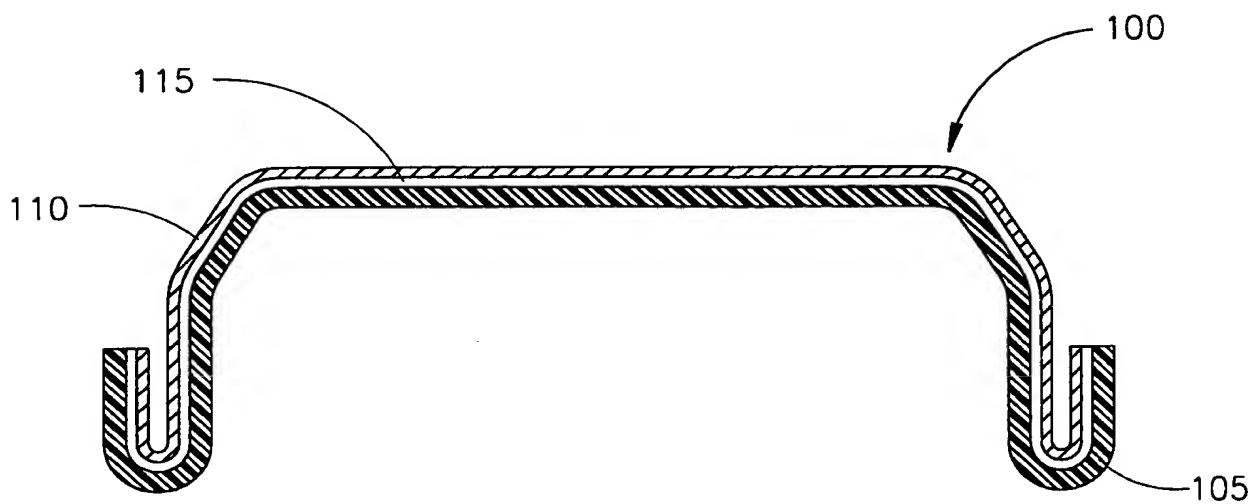


FIG. 5

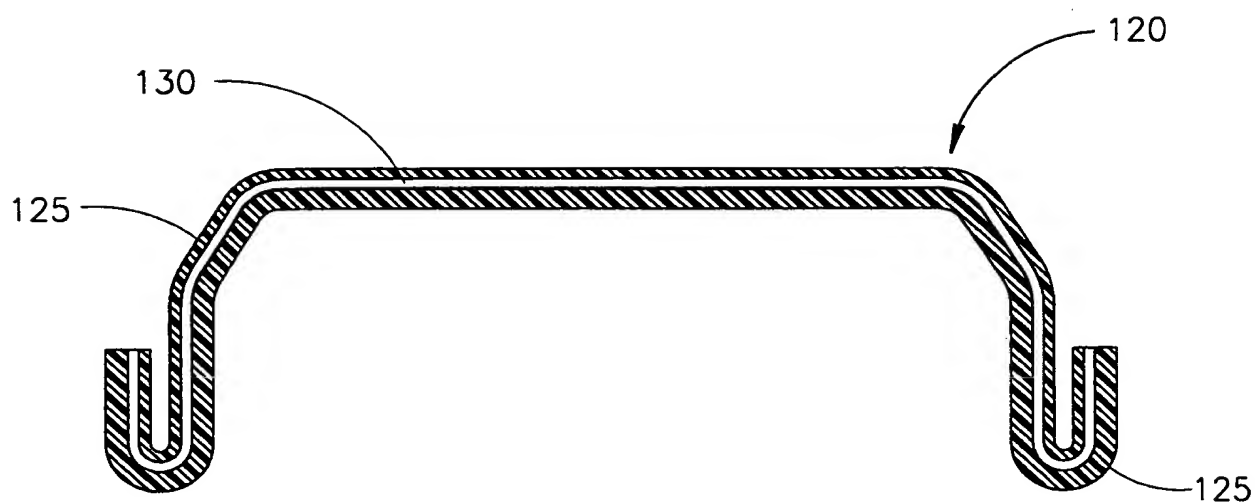


FIG. 6

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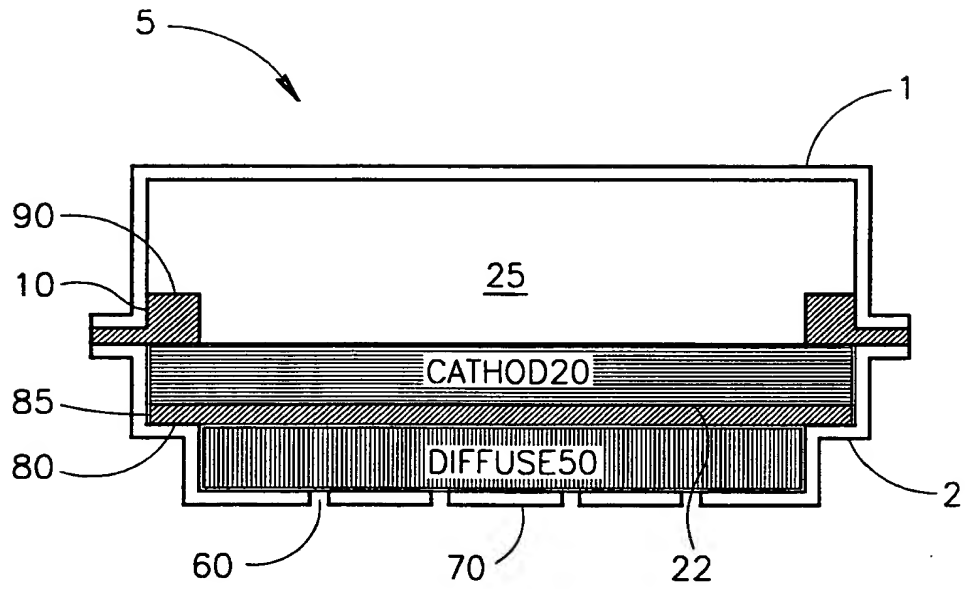


FIG. 7

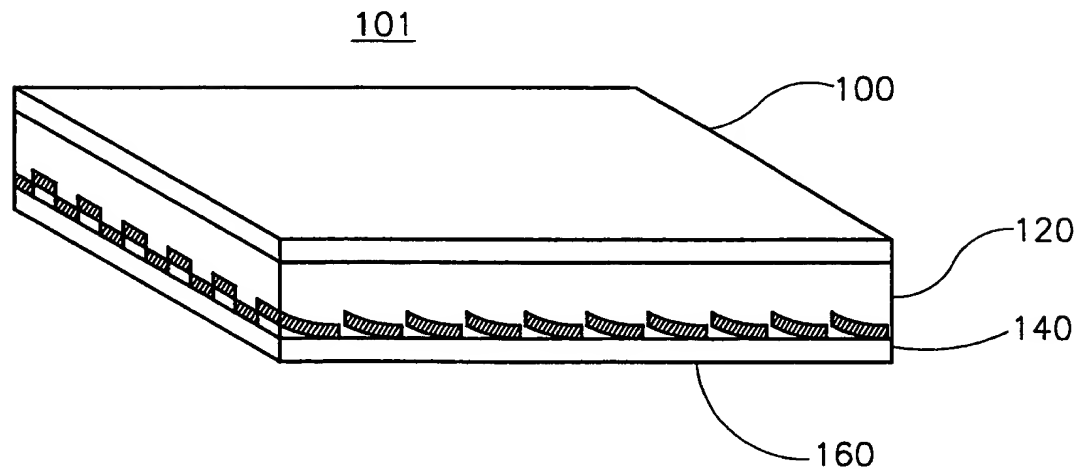


FIG. 8

INTERNATIONAL SEARCH REPORT

International Application No

PCT/IL 99/00681

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 H01M12/06 H01M4/62 H01M8/22 H01M4/90

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	DE 30 25 476 A (GOULD INC., ROLLING MEADOWS, US) 12 February 1981 (1981-02-12)	1,2,7,9, 10,16, 18,19
A	page 12, line 17 -page 17, line 3 figure 1	24
Y	PATENT ABSTRACTS OF JAPAN vol. 010, no. 087 (E-393), 5 April 1986 (1986-04-05) & JP 60 230359 A (PENTEL KK), 15 November 1985 (1985-11-15) abstract	1,2,7,9, 10,16, 18,19
A		11-14, 20-24, 30-37, 39,40
	-/-	

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	DE 36 13 237 A (DURACELL INT., TARRYTOWN, US) 4 December 1986 (1986-12-04) page 3, line 1 - line 4 page 4, line 21 - page 6, line 10 page 10, line 12 - line 27	1-3, 7, 9, 10, 16, 18, 19
A	—	24
Y	DATABASE WPI Section Ch, Week 198152 Derwent Publications Ltd., London, GB; Class L03, AN 1981-95576D XP002131855 & JP 56 145669 A (MATSUSHITA ELEC IND CO LTD), 12 November 1981 (1981-11-12) abstract	1-3, 7, 9, 10, 16, 18, 19
A	—	11-14, 20-24, 30-37, 39, 40
A	DATABASE WPI Section Ch, Week 198540 Derwent Publications Ltd., London, GB; Class L03, AN 1985-246787 XP002131856 & JP 60 163367 A (MATSUSHITA ELEC IND CO LTD), 26 August 1985 (1985-08-26) abstract	1, 2, 4, 9, 10, 16, 18, 19, 21, 23, 27
A	PATENT ABSTRACTS OF JAPAN vol. 008, no. 272 (E-284), 13 December 1984 (1984-12-13) & JP 59 143282 A (MATSUSHITA DENKI SANGYO KK), 16 August 1984 (1984-08-16) abstract	1, 16, 30
A	—	15, 25, 41
A	US 5 232 798 A (GOLDSTEIN JONATHAN ET AL, JERUSALEM, IL) 3 August 1993 (1993-08-03) claim 1	8, 17
A	EP 0 551 204 A (ELECTRIC FUEL LTD, JERUSALEM, IL) 14 July 1993 (1993-07-14) column 8, line 49 - column 9, line 9	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/IL 99/00681

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 3025476 A	12-02-1981	FR 2462784 A GB 2059141 A JP 56022055 A	13-02-1981 15-04-1981 02-03-1981
JP 60230359 A	15-11-1985	NONE	
DE 3613237 A	04-12-1986	US 4585710 A AU 574315 B AU 5550186 A BE 904576 A BR 8601709 A CA 1271216 A CH 671484 A DK 182686 A ES 554197 A FR 2580867 A GB 2174534 A, B IE 57298 B IT 1190322 B JP 2065787 C JP 7032030 B JP 61248371 A MX 164749 B NL 8600928 A NO 861567 A, B, SE 464998 B SE 8601823 A ZA 8602426 A	29-04-1986 30-06-1988 30-10-1986 10-10-1986 16-12-1986 03-07-1990 31-08-1989 23-10-1986 16-07-1987 24-10-1986 05-11-1986 15-07-1992 16-02-1988 24-06-1996 10-04-1995 05-11-1986 22-09-1992 17-11-1986 23-10-1986 08-07-1991 23-10-1986 25-11-1987
JP 56145669 A	12-11-1981	NONE	
JP 60163367 A	26-08-1985	NONE	
JP 59143282 A	16-08-1984	NONE	
US 5232798 A	03-08-1993	NONE	
EP 0551204 A	14-07-1993	IL 100625 A AT 146625 T DE 69306598 D DE 69306598 T ES 2097975 T US 5318861 A	30-03-1995 15-01-1997 30-01-1997 12-06-1997 16-04-1997 07-06-1994



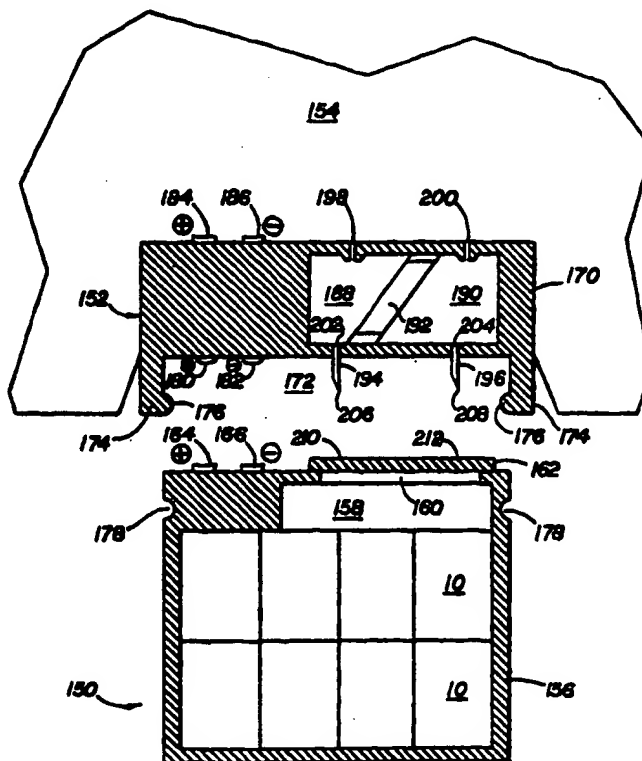
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<p>(21) International Application Number: PCT/US99/30382</p> <p>(22) International Filing Date: 20 December 1999 (20.12.99)</p> <p>(30) Priority Data: 09/216,343 18 December 1998 (18.12.98) US 09/321,352 27 May 1999 (27.05.99) US</p> <p>(71) Applicant: AER ENERGY RESOURCES, INC. [US/US]; 4600 Highlands Parkway, Suite G, Smyrna, GA 30082 (US).</p> <p>(72) Inventors: PEDICINI, Christopher, S.; 405 Saddlebrook Drive, Roswell, GA 30075 (US). WITZIGREUTER, John, D.; 4157 Springhill Lane, Kennesaw, GA 30144 (US).</p> <p>(74) Agents: YOUNG, Jeffrey, E. et al.; Jones & Askew, LLP, 2400 Monarch Tower, 3424 Peachtree Road, N.E., Atlanta, GA 30326 (US).</p>	<p>(81) Designated States: CA, CN, JP, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</p>	

(54) Title: AIR-MANAGING SYSTEM FOR METAL-AIR BATTERY USING RESEALABLE SEPTUM

(57) Abstract

An air-managing system for metal-air battery includes resealable septum and one or more hollow needles. The septum separates air pathway into two segments. One segment is from air cathodes of the battery to the septum and the other is from the septum to the outside air. The needles provide conduits to connect two segments. The septum re-closes its torn portion when the needles are removed. Also disclosed is a reusable air manager including a fan and such needles. The air manager can be coupled to a disposable cell pack which has a septum that can be pierced by the needles.



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**AIR-MANAGING SYSTEM FOR METAL-AIR BATTERY
USING RESEALABLE SEPTUM**

15 Cross-Reference to Related Applications

The following patent applications, all of which are incorporated herein by reference, contain related subject matter and are being filed concurrently with the present application.

20 "CYLINDRICAL METAL-AIR BATTERY WITH A
CYLINDRICAL PERIPHERAL AIR CATHODE"(Attorney Docket 01446-0805);

"AIR MANAGER SYSTEMS FOR METAL-AIR BATTERIES
UTILIZING A DIAPHRAGM OR BELLOWS" (Attorney Docket 01446-0890);

25 "AIR MOVER FOR A METAL-AIR BATTERY UTILIZING A
VARIABLE VOLUME ENCLOSURE" (Attorney Docket 01446-1110);

"DIFFUSION CONTROLLED AIR VENT WITH AN INTERIOR
FAN" (Attorney Docket 01446-0940);

"UNIFORM SHELL FOR A METAL-AIR BATTERY"(Attorney
Docket 01446-1100);

30 "LOAD RESPONSIVE AIR DOOR FOR A METAL-AIR CELL"
(Attorney Docket 01446-1130);

"GEOMETRY CHANGE DIFFUSION TUBE FOR METAL-AIR BATTERIES" (Attorney Docket 01446-1000); and

"AIR DELIVERY SYSTEM WITH VOLUME-CHANGEABLE PLENUM OF METAL-AIR BATTERY" (Attorney Docket 01446-0910).

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Field of the Invention

The present invention relates generally to batteries, and more particularly relates to an air-managing system for a metal-air battery.

10

Description of the Related Art

Metal-air battery cells include an air permeable cathode and a metallic anode separated by an aqueous electrolyte. During discharge of a metal-air battery, such as a zinc-air battery, oxygen from the ambient air is converted at the cathode to hydroxide, zinc is oxidized at the anode by the hydroxide, and water and electrons are released to provide electrical energy. Metal-air batteries have a relatively high energy density because the cathode utilizes oxygen from ambient air as a reactant in the electrochemical reaction rather than a heavier material such as a metal or metallic composition. Metal-air battery cells are often arranged in multiple cell packs within a common housing to provide a sufficient amount of power output. The result is a relatively lightweight battery.

20

To operate a metal-air battery cell, it is necessary therefore to provide a supply of oxygen to the air cathodes of the cells. An air manager system is typically used to provide reactive air and to isolate the air cathodes when the cell is idle. Some prior systems open air cathodes widely to the atmosphere or use a fan system to sweep a flow of new ambient air from openings across the air cathodes to supply oxygen at a rate sufficient to achieve the desired power output. The open air cathodes or the openings are generally sealed during non-use by sealing tapes, plugs, mechanical doors, etc. because the water vapor and oxygen in the ambient air would cause the cell to flood, dry out, or discharge in some circumstances, thereby leading to a reduction in cell efficiency and lifetime. Diffusion-controlling openings have been applied to the air manager, as shown in U.S. Patent

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5,691,074. However, a more strict isolation may sometimes be desired for a longer shelf life.

5 The above-described sealing systems such as a sealing-tape are generally designed for single use and require new sealing means such as a new tape to seal the opening again. Mechanical doors are usually durable and thereby can open and close the openings more than once. The doors typically are positioned on a battery housing case such that a disposable battery body may have door mechanisms, which may be reusable even after the battery loses its power. However, the mechanisms require expensive moving parts and they tend to leak.

10 Thus, there has been a need for a reusable and practical sealing system to prevent water vapor transfer and leakage current when the battery is not in use. The system should be simple and work repeatedly during a battery lifetime, and further minimize disposable parts to lower the cost and to protect the environment. Along these lines, it would be efficient not to have to dispose of an
15 air manager when every cell pack reaches the end of its useful life. If the battery could be divided into a disposable part and a reusable part, a simple and reliable engaging means to connect two parts may be needed.

Summary of the Invention

20 The invention seeks to provide an improved ventilation system and an improved ventilating method for a metal-air cell or battery, which has a long shelf life and retains essentially all its original power during a period of storage.

In accordance with the invention, this object is accomplished in a metal-air power supply system having two air pathway segments separated by a
25 self-sealable septum, and a hollow needle to puncture the septum.

The present invention, therefore, provides a ventilation system for a metal-air battery having a housing or a case for enclosing at least one metal-air cell, at least one self-sealable septum, and one or more hollow needles. The case has at least one opening that is covered with the self-sealable septum and is sealed off
30 from a reactive gas source or the outside air. Thus, the septum divides an air pathway into two segments. The first segment from an air cathode of the cell is

enclosed in the case and terminated by the septum. The second segment to the outside air includes tubular passages of the hollow needles. When the needles penetrate the septum, the two segments are connected and the air pathway is completed to convey a reactive gas, e.g., oxygen, to the air cathode from the outside air.

The present invention provides a multi mode ventilation system for a metal-air battery with one or more openings connected to the outside air in the second segment. At least one air-moving device is disposed in the second segment such that the device may give a satisfactory air flow rate for required power. If the openings are preferably sized, leakage current of the cell may be lowered for non-use conditions when the air-moving device is off. Furthermore, the preferably sized openings prevent the cell from flooding and drying out by exchanging water vapor with the outside air. Thus, the lowest mode is for storage, a middle mode is for non-use, and the highest mode is to provide power with the air-moving device on.

The present invention further provides a power supply system having a cell pack with at least a self-sealable septum and an air-managing device with one or more hollow needles. The cell pack may be stored alone to maintain the original power. The air-managing device engages with the cell pack when the power supply is needed.

The present invention further provides an electric device with an air-managing device and a disposable cell pack with a self-sealable septum. The air-managing device is combined in the electric device such that the consumers may only have to buy a disposable cell pack.

The present invention further provides a cell pack including one or more metal-air cells in a housing which has air opening sealed by resealable septum.

The present invention further provides a reusable ventilation system that engages with an above-mentioned cell pack. The ventilation system has one or more hollow needles, at least one air moving device or fan, and one or more openings for air ingress and egress.

Other features and advantages of the present invention will become apparent upon reviewing the following description of preferred embodiments of the invention, when taken in conjunction with the drawings and the appended claims.

5 **Brief Description of the Drawing**

FIG. 1 is a diagrammatic top view of the cell pack case and the hollow needle embodying the present invention showing position of the cells, the opening, the septum, and the hollow needle, indicating the movement direction of the needle to engage the case.

10 FIG. 2 is a vertical cross sectional view taken along line 2--2 of FIG.1, showing the needle ready to pierce the septum the case.

FIG. 3 is a vertical cross sectional view of the cell pack case engaged by the hollow needle.

15 FIG. 4 is a diagrammatic perspective view of a second embodiment of the present invention showing a cell pack including a septum positioned adjacent to an air manager equipped with hollow needles.

FIG. 5 is a vertical cross sectional view taken along line 5--5 of FIG.4.

20 FIG. 6 is a diagrammatic top view of a cell pack adjacent to an air manager of a third embodiment of the present invention.

FIG. 7 is a diagrammatic top view of a cell pack incorporating an air-moving device, and adjacent to a puncturing device of a fourth embodiment of the present invention.

25 FIG. 8 is a diagrammatic top view of a cell pack and an air-moving device contained in an electric device according to a fifth embodiment of the present.

FIG. 9 is a perspective view of a metal-air battery or a power supply according to a sixth embodiment of the present invention.

30 FIG. 10 is a vertical cross sectional view taken along line 10--10 of FIG.9.

FIG. 11 is a vertical cross sectional view taken along line 11--11 of FIG. 9.

Description of the Preferred Embodiment

5 Referring now in more detail to the drawings, in which like numerals refer to like parts throughout the several views, FIGS 1, 2, and 3 show one embodiment of the present invention. This embodiment is suitable for continuous operation of the cells to provide power and to provide sufficient oxygen to generate the power without a fan. The metal-air battery includes a plurality of
10 cells 10 enclosed within a cell case 12. Since the present invention applies to primary and secondary metal-air cells, the cells of the first embodiment and the following embodiments are similar to those disclosed and known. Suitable components for primary metal-air cells are described in U.S. Patents 5,721,065. Secondary cells also can be used with or without an air mover embodying the
15 present invention, such as that described in U.S. Patent 5,569,551. All types of metal-air cells may benefit by use of the present invention. The figures are exaggerated for illustration. Although the use of the invention with a zinc-air battery is disclosed, this invention should be understood as being applicable to other types of metal-air battery cells. The present invention can be used with
20 primary or secondary batteries.

The case 12 isolates the plurality of cells 10 from the outside air and defines an opening 14 that is covered with a self-sealable septum 16. The cells 10 are generally arranged such that a reactant air plenum 18 is positioned under the
25 cells 10. The air plenum 18 generally defines an air pathway to air cathodes of the cells 10. The septum 16 is affixed at a lower portion of the case 12 and terminates the air pathway at the opening 14. A cell pack 20 includes the cells 10, the plenum 18, the case 12, and the septum 16. The cell pack 20 does not have any air vents.

A hollow needle 22 is positioned so as to puncture the septum 16. The needle 22 may be supported by a board, a case, or the like such that reciprocal
30 longitudinal motion of the needle is enabled. The needle 22 has a needle tip 24, a longitudinal tubular passage 26, and a circular cylindrical wall defining the passage.

The needle 22 is preferably aligned perpendicular to the septum 16 so that a longitudinal motion of the needle 22 toward the septum 16 allows the needle tip 24 to pierce a portion 28 of the septum 16 and the septum material to surround tightly outside of the needle wall for sealing (FIG. 3). Part of the length of the needle 22 is inserted through the septum 16 and the needle is held by the septum material around the needle 22. Thus, the longitudinal tubular passage 26 provides an air pathway to the outside air.

By a longitudinal reverse motion of the inserted needle 22 (FIG. 3), the needle 22 is removed and the septum 16 re-closes and reseals the torn portion 28 to seal off the cell pack 20 from the outside air. This mechanism is similar to that of a vaccine bottle septum from which an inserted hypodermic needle is removed. The needle 22 may be repeatedly re-inserted through the septum 16 and removed from the septum 16 again.

The cell pack 20 may be stored before use or when the cells 10 are inactive. Because the cells 10 are not exposed to fresh air and because leakage current may be minimized, they tend to have a longer shelf life than any cell enclosed by a housing with air vents. When the cell pack 20 is in use or when the cells 10 are active, the hollow needle 22 punctures the septum 16 and the longitudinal tubular passage 26 provides an air pathway to the outside air as described before. Thus, the cells 10 supply enough current to power a load. The present invention, therefore, enables the cells to have a long shelf life and to supply enough power from time to time without using any complicated mechanical doors or any single-use tapes.

The longitudinal tubular passage or hollow portion 26 of the needle 22 is sized to satisfy a load power requirement for oxygen while it limits an air flow rate from the outside air. Thus, the tubular passage diameter may be constructed to allow the air flow. If the needle 22 is too thin, the tubular passage may allow too little air flow. If the needle 22 is too big, it may not be easy for the septum 16 to re-close the tubular passage. If the length is shorter than 1/8", it is difficult for the needle to puncture the septum 16 and/or the tube may not be able to limit the air

flow rate to a desired maximum. If the length is longer than 1/2", it is difficult to handle the needle 22 and to puncture the septum 16 with the needle 22.

Any number of the longitudinal tubular passages 26, that is, any number of needles can be used to satisfy power requirement though FIG.1 shows single needle. Two or more needles may be preferable because one or more inlet and outlet tubular passages may be supplied. By way of example, if the same power as mentioned above is required for the cell pack 20 with two needles, each needle may have a tubular passage from 0.05 to 0.25 square inches in cross-sectional area and from 0.2 to 0.5 inches in length.

The case material is mechanically self-supporting and may be plastic, metal, ceramics, or another generally gas-impermeable material. Some gas permeability through a plastic housing can be tolerated. Materials inert to acid or base may be preferable since most electrolytes are acid or base. The septum 16 is typically made of rubber, a synthetic elastomer, or known compounds that give self-resealing characteristics to the septum 16. Suitable septum material includes that used to protect medicines in vials, such as silicone, PTFE/silicone, natural rubber, butyl rubber, PTFE/natural rubber, PTFE/butyl rubber, fluorocarbon rubber, Viton® etc. These materials are usually gas-impermeable, or hardly have permeability to water, which makes the cell pack well isolated from the outside air or any other reactive gas source and gives it a long shelf life. Further, low permeability prevents a high or low concentration of water vapor in the outside air from flooding or drying out the cells 10.

However, if it is preferable to have a high initial open cell voltage and to prevent consumers from finding that a new cell pack shows a very low voltage, a semi-permeable material may be employed. The semi-permeable material can pass oxygen or a reactive gas so as to keep an open cell voltage of the cells 10 high enough for immediate use. The septum material in this case is typically chosen from silicone rubber or resin, and other oxygen semi-permeable materials.

By way of example, if a typical silicone rubber that has an oxygen permeability coefficient of 19685 ($\text{cm}^3\text{-mm/m}^2\text{ day atm}$) is used for the cell pack 20 with an open area of 6 cm^2 , and if the required leakage current is about 1 ma, then

the required oxygen flow rate is 5.47 cm³/day at 25° Celsius. Thus, the thickness of the septum t may be given by

$$t = 19685 \times 6 \times 10^{-4} \times 0.21 / 5.47 = 0.45 \text{ (mm)}.$$

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It should be understood that the above-mentioned limit of the size of the tubular passages, the opening, the septum, and the case depends on the power requirement and that the power requirement will vary depending upon the electric device to be engaged with the cell pack 20.

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Another embodiment of the present invention is shown in FIGS. 4 and 5. As with the first embodiment, the battery pack 30 is suitable for continuous use while engaged by air-admitting needles. The metal-air battery includes a plurality of cells 10 enclosed within a cell case 32. The figures are exaggerated for illustration. The case 32 defines a cell pack 34 and isolates the plurality of cells 10 from the outside air with the exception of openings 36 that are covered with a self-sealable septum 38. The openings 36 on the bottom surface of the cell pack 34 are defined by grids 40 that may divide each cell 10 and be made of a case material. The grids 40 may mechanically support the septum 38. In this embodiment, there is a small reactant air plenum 42 in the cell pack 34. The septum 38 is affixed on the bottom surface of the cell pack 34 and terminates an air pathway to the outside air at the openings 36. The cell pack 34 therefore does not have any air vents on the cathode side of the separator between the air cathode and the electrolyte.

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A plenum case 44 defines an air plenum box 46 and has a plurality of hollow needles 48 and openings 50. The air plenum box 46 may be positioned and serve as an air collection plenum. The hollow needles 48 having sharp needle tips 52 and longitudinal tubular passages 54 are positioned on the upper surface of the air plenum box 46. Any number of needles at any place of the upper surface may be used to satisfy the power requirement. It is preferable to have one or more needles in each opening 36.

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As described in the first embodiment, the cells 10 are isolated from the outside air to have leakage current minimized and to have a long shelf life when

they are not used, inactive, or in the storage. The plenum box 46 engages with the cell pack so that the needle tips 52 pierce portions 56 of the septum 38 and that the needles 48 penetrate the septum 38 to provide air pathways to an air plenum 58 when the cell pack 34 is in use or the cells 10 are active. The total cross-sectional area of the tubular passages 54 are generally larger than that of the openings 50 so that the total air flow through the tubular passages 54 is larger than that through the openings 50. Therefore, right after the engagement, the current available from the cells 10 increases rapidly consuming a reactive gas, e.g. oxygen, in the plenum 58 and gradually decreases upon using up the stored oxygen. Finally the available current becomes constant and is determined by the air flow rate through the openings 50. Thus, the current characteristics satisfactory for an initial high power requirement of a connected electric device may be controlled by the total cross-sectional areas of the tubular passages 54 and the openings 50, and volume of the plenum 58.

If the steady current needs to be very low, the openings 50 are preferably sized such that their length, i.e., the direction through the thickness of the case 44 is greater than their width, i.e., the direction perpendicular to the thickness of the case 44 such that diffusion of air through the openings 50 may be substantially limited. By "substantially limited," it is meant that the rate of diffusion of oxygen or contaminates through the openings 50 is so slow that humidity transfer is sufficiently small and has little appreciable impact on the efficiency or lifetime of the cell 10 after the output current becomes almost constant.

As described in the first embodiment, the plenum box 46 may be disengaged from the cell pack 34 such that the needles 48 may be removed from the septum 38, which will reseal itself. Thus, the used cell pack may keep its residual power during a period of storage. Further, the septum 38 may be made of a semi-permeable material such that the initial open cell voltage will remain high enough after a long storage as mentioned above. The sizes, the number, and the materials of the case 32, the openings 36, the septum 38, the plenum box 46, the needles 48, their tubular passages 54, and the openings 50 may be preferably varied as

described in connection with the first embodiment. In particular, the needles 48 may preferably be shorter for handling without losing their functions.

5 In the first two embodiments, to protect the cells from flooding or drying out during times when no load is connected to the battery, the battery pack must be disengaged to reseal the septum. Another embodiment is shown in FIG. 6, which has the same cell pack 20 as shown in FIG.1. This embodiment provides a battery pack that can remain engaged with needles through a septum without being subject to flooding or drying out. The features of the cell pack 20 are the same as described in connection with the first embodiment. However, it shows an air
10 manager 60 with an air manager case 62, two needles 70, 72, a fan 80 as an air-moving device, and two diffusion limiting tubes or isolation tubes 82, 84 connected to the outside air through a wall of the case 62.

The air manager is positioned such that the needles 70, 72 can penetrate the septum 16. The needles 70, 72 are hollow and their needle tips 86, 88
15 are sharp to pierce portions 90, 92 of the septum 16 as described in the first embodiment. The needles 70, 72 are positioned on the upper surface of the air manager case 62 such that the air manager may engage with the septum 16 under the cell pack 20. The air manager case 62 is essentially impermeable such that two tubular passages 94, 96 of the needles 70, 72 and the openings 82, 84 are the only
20 pathways to the outside of the case 62. The fan 80 is positioned in the case so as to divide space inside of the case 62 into two chambers 98, 100 and make an air flow and/or pressure difference in the case such that an outlet air flow from the cells through the tubular passage 94 and an inlet air flow to the cells through the tubular passage 96 may occur. Pressurization of the chamber 100 causes air to flow
25 through the tubular passage 96 and also out of the chamber 100 to the outside, through the tube 84. At the same time the low pressure created in the chamber 98 causes air to be drawn from the cells through the tubular passage 94, and make-up air is drawn into the chamber 98 from outside through the tube 82. The make-up air is then re-circulated between the air manager and the cells.

30 The sizes of the tubular passages 94, 96 are generally larger than those of the openings 82, 84 such that an air flow resistance of the tubular passages

94, 96 may be smaller than that of the openings 82, 84. Thus, more air generally moves through the tubular passages 94, 96 in the re-circulation process.

When the cell pack 20 is not engaged with the air manager, the cell case 12 and the septum 16 isolate the cells 10 such that the cells 10 have a long shelf life. When the cells 10 are in use or are active, the air manager 60 engages with the cell pack 20 with the needles 70, 72 penetrating the septum 16 to about halfway along their length. Thus, the tubular passages 94, 96 provide air pathways from the air cathodes (not shown) of the cells 10 to the chambers 98, 100 of the air manager 60. If the chambers 98, 100 are large and filled with a reactive gas and if the tubular passages 94, 96 are wide, the initial available current characteristics are similar to those described in connection with the second embodiment. Since the openings 82, 84 are diffusion limiting tubes, the cells 10 may have a long shelf life when the fan 80 is off, even when the septum remains pierced by the needles 70, 72. The tubular passages 94, 96 could alternatively be the diffusion limiting tubes in a way of isolating the cells 10.

The diffusion limiting tube may be referred to as an isolating passageway or a diffusion limiting passageway due to its isolating capability. In accordance with an example in US Patent 5,691,074, the diffusion limiting passageways function to limit the amount of oxygen that can reach air cathodes to minimize the self discharge and leakage or drain current of a metal-air cell.

The diffusion limiting passageways 82, 84 (or alternatively 94, 96) also minimize the detrimental impact of humidity on the metal-air cell, when the fan 80 is not forcing air flow through the diffusion limiting passageways 82, 84 (or alternatively 94, 96). A metal-air cell that is exposed to ambient air having a high humidity level may absorb too much water through its air electrode and fail due to a condition referred to as "flooding". Alternatively, a metal-air cell that is exposed to ambient air having a low humidity level may release too much water vapor from its electrolyte through the air electrode and fail due to a condition referred to as "drying out".

The efficiency of the isolating or diffusion limiting passageway in terms of the transfer of air and water into and out of a metal-air cell can be described

in terms of an "isolation ratio". The "isolation ratio" is the ratio of the rate of water loss or gain by a cell while its oxygen electrodes are fully exposed to the ambient air, as compared to the rate of the water loss or gain of the cell while its oxygen electrodes are isolated from the ambient air, except through one or more limited openings, that is, diffusion limiting passageways. For example, given identical metal-air cells having electrolyte solutions of approximately thirty-five percent (35%) KOH in water, an internal relative humidity of approximately fifty percent (50%), the ambient air having a relative humidity of approximately ten percent (10%), and no fan-forced circulation, the water loss from a cell having an oxygen electrode fully exposed to the ambient air should be more than 100 times greater than the water loss from a cell having an oxygen electrode that is isolated from the ambient air, except through one or more diffusion limiting passageways. In this example, an isolation ratio of more than 100 to 1 should be obtained.

More specifically, each of the diffusion limiting passageways 82, 84 (or alternatively 94, 96) preferably has a width that is generally perpendicular to the direction of flow therethrough, and a length that is generally parallel to the direction of flow therethrough. The length and the width are selected to substantially eliminate air flow and diffusion through the diffusion limiting passageways 82, 84 (or alternatively 94, 96) while the air moving device is not forcing air flow through the diffusion limiting passageways 82, 84 (or alternatively 94, 96). The length is greater than the width, and more preferably the length is greater than about twice the width. The use of larger ratios between length and width are preferred. Depending upon the nature of the metal-air cells, the ratio can be more than 200 to 1. However, the preferred ratio of length to width is about 10 to 1.

The isolating or diffusion limiting passageways 82, 84 (or alternatively 94, 96) could form a portion of the air path must take between the ambient and the oxygen electrodes. Each of the diffusion limiting passageways 82, 84 (or alternatively 94, 96) may be defined through the thickness of the case 62, but preferably they are in the form of tubes as described above.

In general, the diffusion limiting passageways may be cylindrical, and for some applications each can have a length of about 0.3 to 2.5 inches or

longer, with about 0.88 to 1.0 inches preferred, and an inside diameter of about 0.03 to 0.3 inches, with about 0.09 to 0.19 inches preferred. The total open area of each diffusion limiting passageway for such applications, measured perpendicular to the direction of flow therethrough, is therefore about 0.0007 to 0.5 square inches. In other applications, the diffusion limiting passageways each can have a length of about 0.1 to 0.3 inches or longer, with about 0.1 to 0.2 inches preferred, and an inside diameter of about 0.01 to 0.05 inches, with about 0.15 inches preferred. The preferred dimensions for a particular application will be related to the geometry of the passageways and the cathode plenums, the particular air mover utilized, and the volume of air needed to operate the cells as a desired level.

By way of example, in a preferred embodiment of a cell pack 20 designed to power a portable computer (not shown), a 6-volt battery with 6 cells 10 is used. Each cell 10 has an output of about 1 volt or slightly higher at about 1 to 4 amps. Each cell 10 has an exposed cathode area (not shown) of about 18 to 22 square inches for a total exposed cathode area of about 108 to 132 square inches. The battery therefore has a current density of about 50 to 200 ma per square inch of cathode surface. In order to satisfy this power requirement, an air flow from 33 to 200 cubic inch/min is needed.

The diffusion limiting passageways are not necessarily cylindrical, as any cross-sectional shape that provides the desired isolation is suitable. The isolating passageways need not be uniform along their length, so long as at least a portion of each diffusion limiting passageway is operative to provide the desired isolation. Further, the diffusion limiting passageways may be straight or curved along their length. In fact, a diffusion limiting passageway may be formed by a gap between spaced apart two-dimensional surfaces, so long as the air molecules must follow a sufficiently restricted path to move from the ambient air to the air cathode. Other exemplary diffusion limiting passageways and systems are disclosed in U.S. Patent No. 5,691,074 and U.S. Application No. 08/556,613, and the entire disclosure of each of those documents is incorporated herein by reference.

Referring again to FIG. 6, when the fan 80 is turned on, a relatively large amount of air flow comes from the outside of the air manager case 62 through

the opening 82, mixes with air flow coming through the tubular passage 94, and goes into the plenum 18 through the tubular passage 96 and out of the case 62 through the opening 84. Thus, the cell pack can supply a connected electric device with required power. The fan's rotational speed may be adjusted to supply the required power. The fan is operated with power from the cells 10, and is connected by leads and terminals not shown in FIG. 6.

Since the openings 82, 84 are diffusion limiting passageways, air flow through the passageways 82, 84 may be more quantitative. The passageways 82, 84 are, thereby, preferably constructed and arranged to allow a sufficient amount of air flow therethrough while the air moving device or the fan 80 is operating so that a sufficient output current, typically at least 50 ma, and preferably at least 130 ma can be obtained from the metal-air cells 10. In addition, the diffusion limiting passageways 82, 84 are preferably constructed to limit the air flow and diffusion therethrough such that the drain current that the metal-air cells are capable of providing to a load while the fan 80 is not forcing air flow through the passageways 82, 84 is smaller than the output current by a factor of about 50 or greater. Thus, when the fan 80 is off and the humidity level within the cell is relatively constant, only a very limited amount of air diffuses through the passageways. The water vapor within the cell protects the air cathodes (not shown) from exposure to oxygen. The air cathodes are sufficiently isolated from the ambient air by the water vapor such that the cells 10 have a long shelf life without sealing the passageways 82, 84 with mechanical air doors or the like. In addition, the diffusion limiting passageways 82, 84 are preferably constructed to provide the isolation ratio of more than 50 to 1.

When the air manager 60 is disengaged from the cell pack 20, the cells 10 are essentially isolated from the outside air, and the drain current can be as low as the storage modes before first use of the cell pack 20. With the help of the semi-permeable septum 16, an initial open cell voltage may be maintained. When the air manager 60 engages the cell pack 20, the openings 82, 84 may be the only air pathways to the outside air and the drain current mode with the fan off is reduced as described above. When the fan is turned on, the current to a load can be

varied between several modes adjusted by the fan speed control to satisfy the power requirement.

Since the air manager 60 may be reusable with other cell packs even after the cell pack 20 discharges its energy, it is possible to minimize disposable parts. The sizes, the number, and the materials of the case 12, the openings 14, the septum 16, the plenum 18, the air manager case 62, the needles 70,72, their tubular passages 94,96, the chambers 98, 100, the fan 80, and the openings 82, 84 may be preferably changed as described in connection with similar parts used in the earlier embodiments.

In particular, if the needles 70,72 are large such that their tubular passages 94,96 may be larger than the diffusion limiting tubes, the fan 80 may inhale more air flow from the outside. Thus, the air cathode is exposed to air including higher concentration of oxygen so that the battery may supply more energy when the fan 80 is on. On the other hand, when the fan 80 is off and the air manager 60 engages with the cell pack 20, that is, when the battery is temporarily inactive, the cells are less isolated from the ambient air that may have a high or low humidity level so that the cells 10 are more likely to fail due to a condition referred to as "flooding" or "drying out" as described before. This may be prevented, if the air manager 60 is disengaged from the cell pack 20 such that the air passageways are re-closed by the septum 16.

Another embodiment of a cell pack 110 according to the present invention is shown in FIG. 7. A cell pack case 112 encloses cells 10, a reactive air plenum (not shown), and an air manager portion including two chambers 114, 116 separated by a fan 118. An opening 120 connects the chambers 114, 116 to the plenum. An opening 122 extends across both chambers 114, 116 and is covered with a septum 124 and sealed off from the outside air. The air manager is an air-moving device having the fan 118 to make air flow and/or pressure difference between two chambers 114 and 116. Two needles 126, 128 secured to a needle board 130 are positioned so as to puncture portions 132, 134 of the septum 124. The needles 126, 128 have sharp needle tips 136, 138 and tubular passages 140, 142 as described in the other embodiments.

When the cells 10 are not in use or inactive, the needles 126, 128 are apart from the septum 124 and cell isolation is maximized as described above. If the septum 124 is made of a semi-permeable material, a satisfactory initial open cell voltage may be maintained during storage. When the cells 10 are in use or active, the needles 126, 128 penetrate the septum 124 at portions 132, 134 to provide air pathways from air cathodes (not shown) of the cells to the outside air. When the fan is turned on, the air is circulated with make-up fresh air through the tubular passages 140, 142 and the load current is adjusted by varying the fan speed to satisfy a high power requirement of a connected electric device.

If the cell pack must be well isolated when the fan is off, the tubular passages may be sized to be diffusion limiting isolation tubes as described above. When the needles 126, 128 are apart from the septum 124, the cells 10 are essentially isolated from the outside air and the drain current may be minimized to as low a mode as the storage modes existing before first use of the cell pack 110. With the help of the semi-permeable septum 124, an initial open cell voltage may be maintained. When the needles 126, 128 penetrate the septum 124 at portions 132, 134, the tubular passages 140, 142 may be the only air pathways to the outside air and the drain current mode with the fan off is reduced as described above. When the fan is turned on, the current to a load can be varied between several modes adjusted by the fan speed control to satisfy the power requirement.

In this embodiment, a small part such as the needle board 130 can start the cell pack so as to be a switch without any electrical contacts, and provide power to a battery-preinstalled electric device. The sizes, the number, and the materials of the case 112, the openings 120, 122, the septum 124, the plenum (not shown), the chambers 114, 116, the fan 118, the openings 120, 122, the needles 126, 128, their tubular passages 140, 142, and the board 130 may preferably be changed for the purposes described above.

Another embodiment is shown in FIG. 8, which includes a cell pack 150, and an air-managing head 152, mounted in an electric device 154. The cell pack 150 includes a case 156, cells 10, a reactive air plenum below the cells (not shown), and an extra plenum 158, adjacent to an opening 160 covered by a septum

162. A pair of terminals 164, 166 connected to positive and negative leads (not shown) from the cells 10 are positioned on the exterior of the case 156 facing the air-managing head 152. The case 156 isolates the cells from the outside air with the help of the septum 162 as described in the other embodiments. The extra plenum 158 may diffuse and mix fresh and residual air inside of the case 156 and supply each air cathode evenly with reactive gas, i.e., oxygen. In the alternative, the extra plenum may be omitted, in which case the needles are directed into the reactive air plenum. If the septum 162 is made of a semi-permeable material, an initial open cell voltage may be maintained during storage.

The air-managing head 152 includes a case 170, which defines an outwardly facing rectangular recess 172 for receiving the cell pack 150. Two engaging arms 174 with knobs 176 define the recess to receive and engage with a portion of the cell pack 150. Two recesses 178 on opposite exterior walls of the cell pack case 156 receive the knobs 176 with force caused by elastic bending of the arms 174 in a similar way as a ratchet mechanism. Two terminals 180, 182 are positioned on a back wall of the recess 172 to engage the terminals 164, 166, respectively. Two electrical terminals 184, 186 or hard wiring are provided on the other side of the head 152 to supply the electric device 154 with electrical power from the cell pack 150.

Two chambers 188, 190 are formed in the air-managing head 152 separated by an air mover such as a fan 192. A needle 194 extends out from the chamber 188 and a needle 196 extends out from the chamber 190. The chambers 188, 190 are connected to outside air through tubes 198, 200, respectively. The tubes 198, 200 (shown diagrammatically) preferably are diffusion limiting isolation tubes of the type described above, and the needles 194, 196 have larger openings 202, 204 designed for free air flow rather than isolation purposes.

Thus, the cell pack 150 is removably held by the air-managing head 152 coinciding with the needles 194, 196 penetrating the septum 162. The needles 194, 196 have sharp needle tips 206, 208 to pierce portions 210, 212 of the septum 162 and the tubular passages 202, 204 to provide air pathways between air cathodes (not shown) of the cells 10 and the two chambers 188, 190.

5 The fan 192 makes an air flow and/or pressure difference between two chambers 188 and 190, the fan 192 being disposed in-between. The openings 198, 200 communicate with the outside air or a reactive gas source such that the reactive gas, e.g., oxygen can come through one of the openings 198, 200 and one of the tubular passages or openings 202, 204 to reach the air cathodes of the cells 10, in a manner described above.

10 In this embodiment, the air-managing head 152 is installed in the electric device 154 such that the consumers need only buy the cell pack 150. The cell pack can be stored in completely sealed conditions with an impermeable septum 162 or an impermeable tape (not shown) can be affixed on a semi-permeable septum 162. In the latter case, retail stores may stock the cell pack 150 after removing the tape or consumers may remove the tape sometime before use, so that the cell pack has a satisfactory initial open cell voltage. The sizes, the number, and the materials of the case 156, the opening 160, the septum 162, the plenum (not shown), the extra plenum 158, the chambers 188, 190, the fan 192, the openings 15 198, 200, the needles 194, 196, their tubular passages 202, 204, and other parts may preferably be changed as described above.

20 Another embodiment is shown in FIGS. 9, 10, and 11. A cylindrical metal-air battery or power supply has an air-managing head 220 and a cell pack 222 like the embodiment shown in FIG. 6. The air-managing head 220 has a cylindrical coupling 224, an outer case 226, two openings 228, 230, and a positive terminal 232. The cell pack has a negative terminal 234, an outer case 236, and a coupling portion 238 with two positive terminals 240, two negative terminals 242, and an elongate self-sealable septum 244.

25 The air-managing head 220 further includes two positive terminals 246 disposed inside of the circular cylinder 224 opposite to each other, two negative terminals (not shown) disposed inside of the circular cylinder 224 in orthogonal positions to the positive terminals 246, two hollow needles 248, 250 parallel to the axial direction of the battery, two chambers 252, 254 divided by a fan 30 256, and a fan controller 258.

5 The two chambers 252, 254 are defined with a circular plate 260 and other walls, and formed in the air-managing head 220 separated by an air mover such as the fan 256. The needle 248 extends out from the chamber 252 and the needle 250 extends out from the chamber 254. The chambers 252, 254 are connected to outside air through openings 228, 230, respectively. The openings 228, 230 (shown diagrammatically) preferably are diffusion limiting isolation tubes of the type described above, and the needles 248, 250 have larger openings 262, 264 designed for free air flow rather than isolation purposes.

10 The cell pack 222 further includes two cells having anode gels 266, anode containers 268, air cathodes 270, insulating end plates 272, 274, 276, current collectors and leads 278, 280, and an air plenum 282. The end plate 276 has a slit opening covered with the elongate septum 244. The two negative terminals 242 are connected to the anode containers 268 with leads 280. The two positive terminals 240 are connected to current collectors (not shown) of the air cathodes 270 with leads (not shown). These four terminals are positioned on the exterior circular periphery of the coupling portion 238 so as to connect to corresponding terminals inside of the cylindrical coupling 224 of the air-managing head 220 in order to supply the fan 256 with electric power. The positive terminal 232 of the power supply is also connected to the terminals 246 with leads (not shown). The fan controller 258 also is connected to control the supply of electric current from the cell pack 222 to the fan 256. If the elongate septum 244 is made of a semi-permeable material, a satisfactory initial open cell voltage may be maintained during storage.

25 The cell pack 222 may be removably held by the air-managing head 220 coinciding with the needles 248, 250 penetrating the elongate septum 244. To selectively lock the cell pack 222 to the head 220, a connector (not shown) may be provided, such as the knobs and recesses of the previous embodiment. The needles 248, 250 have sharp needle tips 284, 286 to pierce portions 288, 290 of the septum 244, and the tubular passages 262, 264 provide air pathways from air cathodes 270 of the cells to the two chambers 252, 254.

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The fan 256 makes an air flow and/or pressure difference between two chambers 252 and 254. The openings 228, 230 communicate with the outside air such that oxygen can come through one of the openings 228, 230 and one of the tubular passages 262, 264 to reach the air cathodes 270 of the cells, in a manner described above.

5 In this embodiment, the air-managing head 220 is separable for re-use such that the consumers need only buy the cell pack 222. The cell pack can be stored in completely sealed conditions with an impermeable septum 244 or an impermeable tape (not shown) can be affixed on a semi-permeable septum 244. In
10 the latter case, retail stores may stock the cell pack 222 after removing the tape or consumers may remove the tape sometime before use, so that the cell pack has a satisfactory initial open cell voltage. The sizes, the number, and the materials of the case 236, the septum 244, the plenum 282, the chambers 252, 254, the fan 256, the
15 openings 228, 230, the needles 248, 250, their tubular passages 262, 264, and other parts may preferably be changed as described above. In particular, the cylindrical coupling 224 may be formed in the same size as the outer case 226 such that the whole battery is formed in a regular battery size such as "AA".

20 The above description is that of preferred embodiments of the invention. Various alterations and changes can be made without departing from the spirit and broader aspects of the invention as set forth in the appended claims, which are to be interpreted in accordance with the principles of patent law, including the Doctrine of Equivalents.

Claims

What is claimed is:

- 5 1. A metal-air power supply system comprising:
 an enclosure surrounding one or more metal-air cells each
including an air electrode;
 a structure providing a first air pathway segment within the
enclosure from the air electrode to a puncturable, resealable septum comprising at
10 least a portion of the enclosure surrounding said cell;
 a hollow needle forming a portion of a second air pathway
segment connected to a source of reactive gas and positioned such that said needle
is capable of puncturing the septum.
- 15 2. The metal-air power supply system of claim 1 further
comprising at least one diffusion limiting passageway in said second air pathway
segment.
- 20 3. The metal-air power supply system of claim 2 wherein said
diffusion limiting passageway is defined by said needle.
4. The metal-air power supply system of claim 2 further
comprising at least one air-moving device in said air pathway.
- 25 5. The metal-air power supply system of claim 4 wherein said
air-moving device is disposed between said needle and said diffusion limiting
passageway.

6. The metal-air power supply system of claim 1 further comprising:

at least one inlet diffusion limiting passageway and at least one outlet diffusion limiting passageway in said second air pathway segment; and
at least one air-moving device in said air pathway.

7. The metal-air power supply system of claim 6 wherein said air-moving device is disposed between said needle and said diffusion limiting passageway.

8. The metal-air power supply system of claim 1 further comprising:

at least one diffusion limiting passageway in said second air pathway segment communicating with said hollow needle and a reactive gas source;
and

at least one air-moving device in said first air pathway segment between said air electrode and said septum.

9. The metal-air power supply system of claim 8, wherein said septum comprises a membrane semi-permeable to said reactive gas.

10. The metal-air power supply system of claim 1, wherein said septum comprises a membrane semi-permeable to said reactive gas.

11. The metal-air power supply system of claim 1 further comprising at least one air-moving device between said air electrode and said septum.

12. A metal-air cell pack comprising:
a housing containing one or more metal air cellss and
defining a reactive air plenum associated with air electrodes of said cells; and
a pierceable, resealable septum forming a portion of an
5 exterior wall of said housing, said septum being connected with said plenum by an
air pathway.

13. A ventilation system for metal-air cells, comprising:
an air moving device within an enclosure;
10 one or more ventilation openings in said enclosure allowing
entry of outside air; and
one or more hollow needles extending outwardly from said
enclosure.

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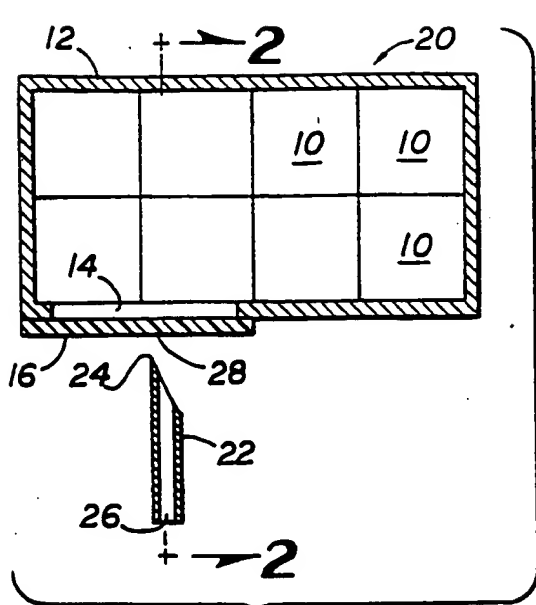


FIG 1

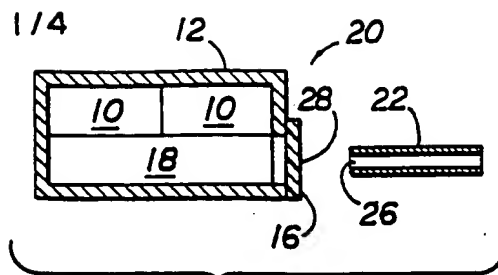


FIG 2

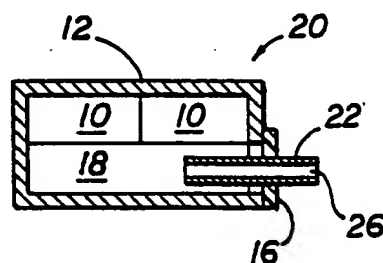


FIG 3

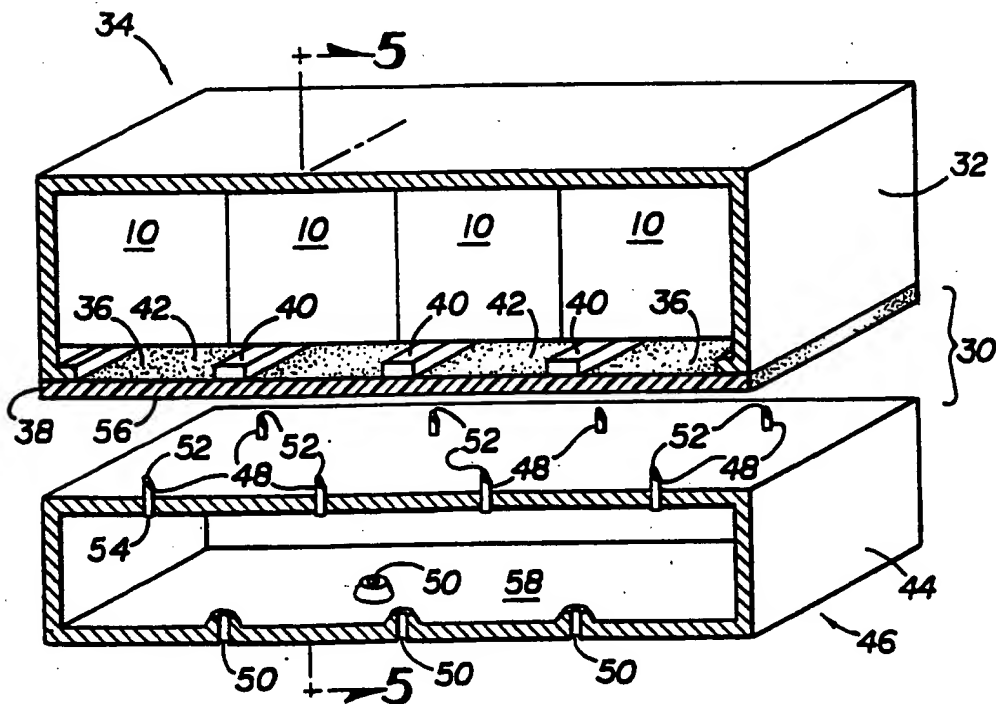
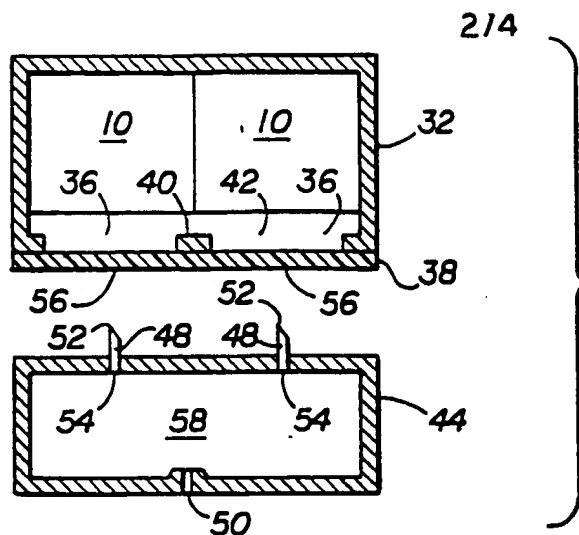
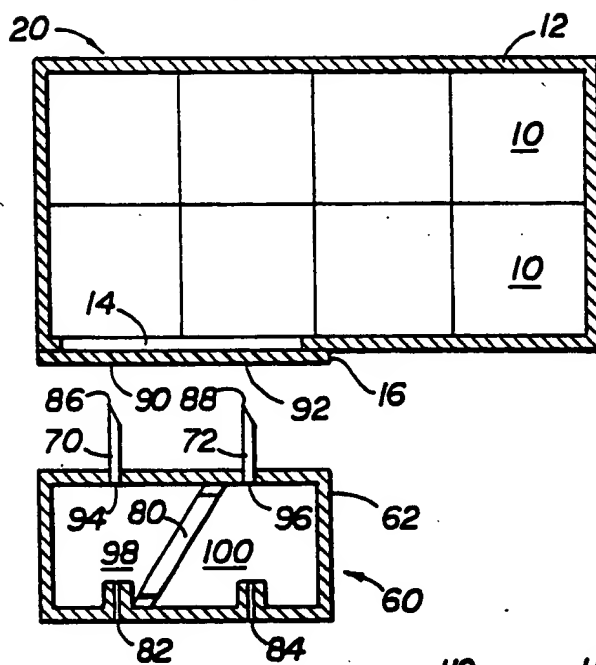
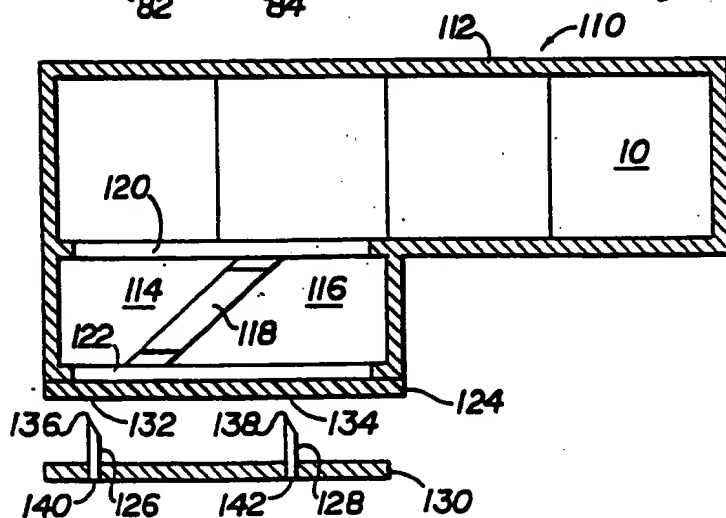
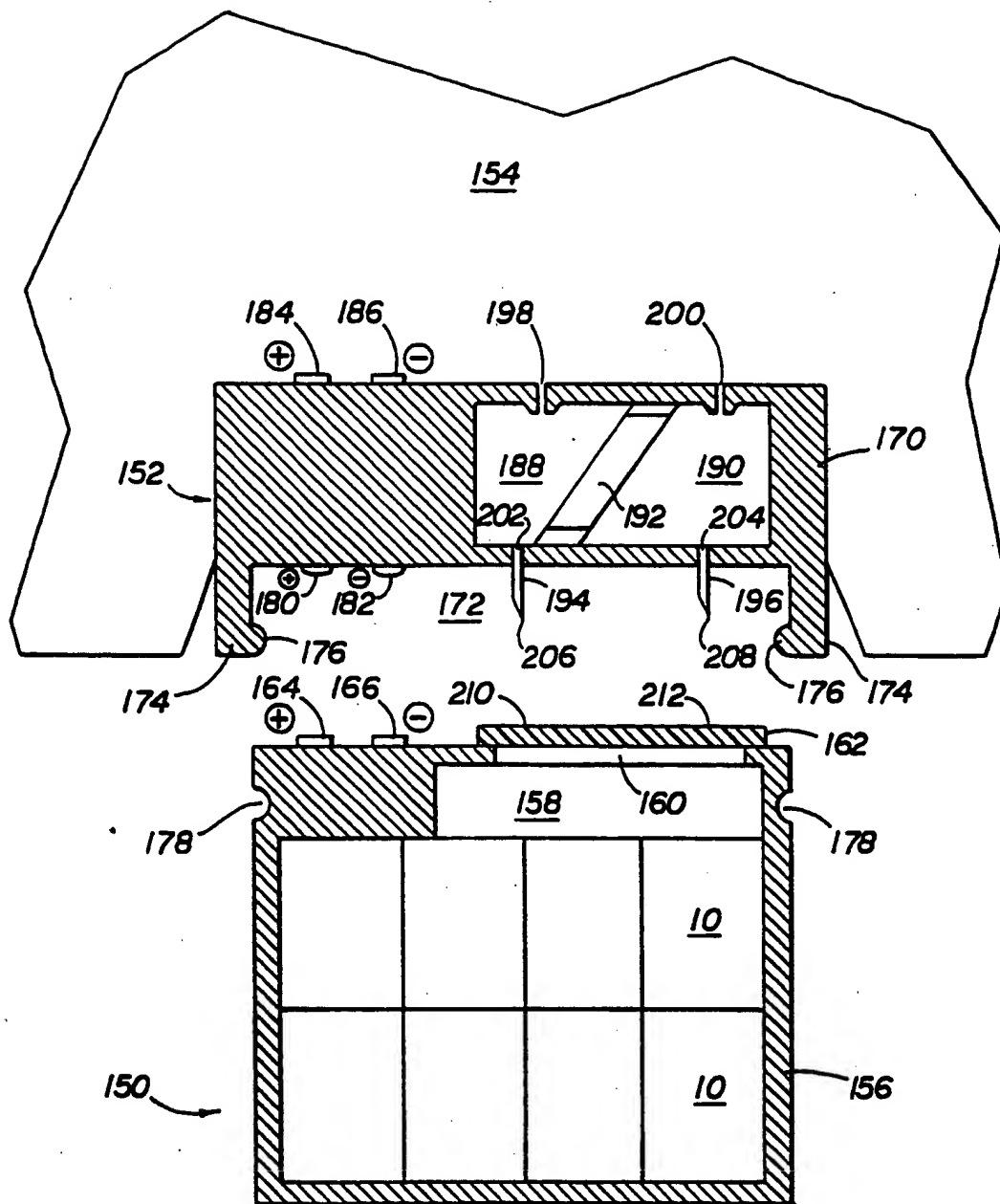


FIG 4

**FIG 5****FIG 6****FIG 7**

3 / 4

**FIG 8**

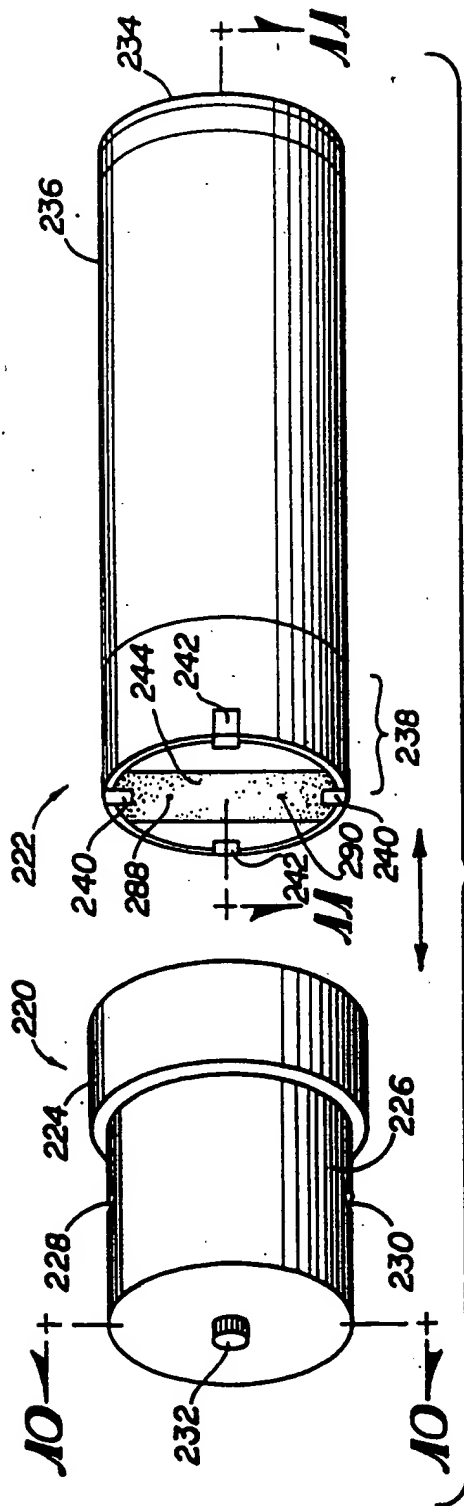


FIG 9

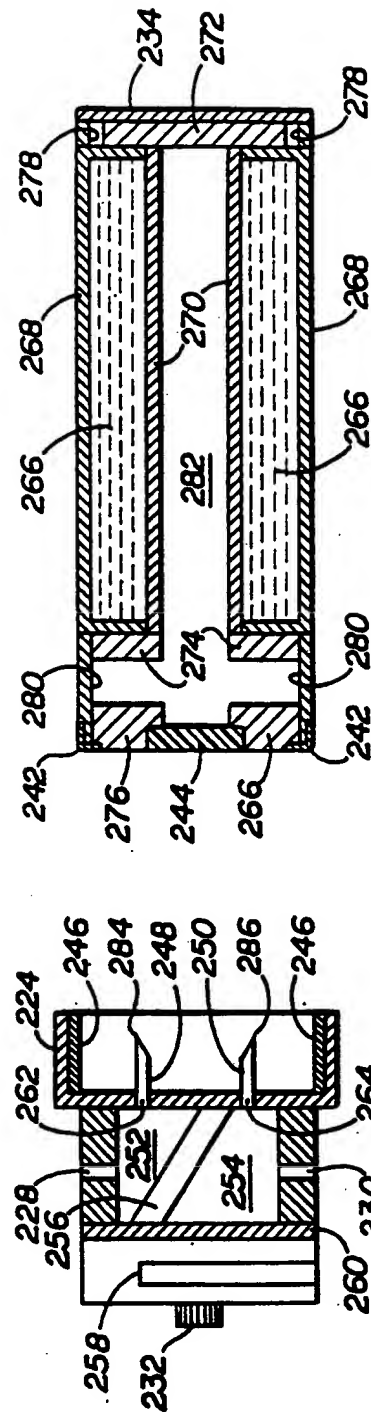


FIG 1A

FIG 10

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 99/30382

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 H01M12/06 H01M2/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 691 074 A (PEDICINI CHRISTOPHER S) 25 November 1997 (1997-11-25) cited in the application column 3, line 66 - column 4, line 43 figure 1	1,2,4-6, 8,12,13

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"A" document member of the same patent family

Date of the actual completion of the international search

15 May 2000

Date of mailing of the international search report

22/05/2000

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Peis, S

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/30382

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5691074 A	25-11-1997	AT 189343 T	15-02-2000
		AU 7451296 A	07-05-1997
		DE 69606423 D	02-03-2000
		EP 0860032 A	26-08-1998
		JP 11508728 T	27-07-1999
		WO 9715090 A	24-04-1997
		US 5919582 A	06-07-1999